

IEA Hydrogen Implementing Agreement
Annex 22 – Fundamental and applied hydrogen storage materials development 2009 - 2012
Project Plan

Project No.

Title: Light metals and porous materials for hydrogen storage.

Project Leader: Craig BUCKLEY (Department of Imaging and Applied Physics, Curtin University) – Australia.

International Collaborations: Professor Bjorn Hauback, Institute for Energy Technology, Norway. Associate Professor Torben Jensen, Aarhus University, Denmark

Level of Effort (Duration): 1.5 py/y (3 years)

Background

Australia joined Task 17 on June 1, 2004 and has been involved in Task 17 and Task 22 since that date. The Australian representatives are Evan Gray and Craig Buckley. I have regularly attended Task 17 and Task 22 Workshops since October 2005. The research conducted by my research group during this period mainly concentrated on the hydrogen storage and structural properties of Al, Mg and carbon aerogels (CA). I have been working in the hydrogen storage and structural properties of materials research fields since 1989 and since 1992 have published 60 refereed Journal papers.

Project Plans

In this project the research will continue to concentrate on synthesizing nanoparticles of Al, Mg and their alloys and to test their hydrogen storage properties. Theoretical work suggests that a reduction in Mg particle size below 10 nm can result in thermodynamic destabilization of the hydride phase with a consequent lowering of the desorption temperature. This effect is expected to be pronounced for particles below 3 nm in diameter. It is therefore important to experimentally test the theoretical predictions. Our recent work has shown that a MgH₂ particle size of ≈ 7 nm lowers the desorption temperature by 6 K when compared to that of the bulk. We have also shown that the reduction in the desorption temperature due to the change in reaction enthalpy (ΔH) is less than that expected from theoretical studies due to the counteracting decrease in reaction entropy (ΔS). We will endeavour to decrease the particle size further so that size dependent theoretical predictions of the thermodynamic properties can be tested with experimental results. Research on synthesizing Al and alane nanoparticles will continue so that theoretical predictions of the thermodynamics of these materials can be tested with experiment. The aim in this case is to measure the change in absorption pressure as the particle size decreases. Several publications have resulted from the Task 22 (2006 – 2009) research concerning the above.

Several refereed journal articles on the hydrogen storage properties of carbon aerogels (CA) have been published by my research group over the past 2 years. Excellent hydrogen capacities of up to 5.2 wt.% have been published and future research will concentrate on encapsulating MgH₂, Mg, Al and alane nanoparticles within a nanoporous CA matrix. The aim of this is to produce high wt.% storage capacities at higher temperatures than 77 K, preferably room temperature. To achieve this aim the enthalpy of the CA (≈ 5 kJmol⁻¹) needs to be raised to $\approx 15 - 20$ kJmol⁻¹.

Using hydrogen in stationary applications or as a future fuel or a fuel additive for sea transport is a huge market, and given that weight is not an issue in these applications an inexpensive intermetallic with the requisite pressure, temperature and kinetic characteristics has the potential to be a suitable hydrogen storage material for this market. Therefore research will be conducted on intermetallics comprising of Al, Mg or both (due to their plentiful supply and low cost) in an effort to find a suitable compound that will absorb and release hydrogen under suitable pressure, temperature and kinetic conditions. We have chosen to research the hydrogen storage properties of a number of intermetallics containing Al, Mg or both, because a hydrogen storage material for a large ship (due to the quantity of fuel required) will weigh in

the order of tonnes, hence relatively inexpensive materials will be required to keep the cost of the hydrogen storage material at a commercial level.

The research will be conducted in close collaboration with Professor Evan Gray, members of the National Hydrogen Material Alliance in Australia and international researchers.

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Project No.

Title: In-situ studies of hydrogen storage materials with neutrons and x-rays

Project Leader: Evan GRAY (Queensland Micro- and Nanotechnology Centre, Griffith University) – Australia

International Collaborations: Torben Jensen (University of Aarhus, Denmark), Craig Jensen (University of Hawaii, USA), Ewa Rönnebro (Pacific Northwest National Laboratory, USA), Bill David (ISIS/University of Oxford, UK)

Level of Effort (Duration): 1 py/y (3 years)

Background

Evan Gray, Jim Webb and colleagues at Griffith University focus on the use of in-situ beam techniques (neutrons, x-rays and muons) to elucidate the mechanisms and pathways by which hydrogen is absorbed and desorbed by potential storage materials. The most-used technique is powder diffraction, by which means the progress of a reaction can be followed, often in real time, via the crystallography of the reacting phases. A lot of effort has been put into learning how to extract the true sample scattering from the measured intensity, which may include a strong contribution from the sample cell. Careful attention to correction for background intensity from the instrument and sample environment is necessary to be able to perform Rietveld profile analysis on the diffraction profiles and further allows diffuse scattering from nanocrystalline or nearly-amorphous phases to be measured. A vital feature of our approach is accurate measurement of the amount of H or D in the sample during the diffraction measurement. This provides a link to measurements on the same material by other techniques and, importantly, an absolute reference point for Rietveld profile analysis by independently determining the total H/D occupancy of the sample.

Our partners have superb complementary expertise in materials synthesis, analytic techniques including NMR and Raman spectroscopy, and diffraction techniques.

The materials of interest are those synthesised from the lightest elements, from lithium to aluminium.

Project Plans

The focus of the proposed research is in-situ structural studies of materials under hydrogen (protium or deuterium as appropriate) at gas pressures up to 2000 bar and temperatures from cryogenic to at least 600°C.

An important part of the project is the continued development of reliable methodologies and instrumentation for in-situ studies of hydrogen storage materials under hydrogen gas pressure using neutron and synchrotron x-ray beams. We are presently able to perform neutron powder diffraction measurements under deuterium pressures exceeding 2000 bar at the ISIS spallation source in the UK. With the advent of the Australian OPAL reactor source and the availability there of first-class powder diffraction instruments, we will have a significantly greater and easier access to beam time for such studies. A cell for 2000-bar deuterium will be available, in addition to cells for lower pressures.

In-situ x-ray powder diffraction is already performed by Torben Jensen and colleagues up to about 200 bar hydrogen pressure. Based on this approach (sample cell is a sapphire capillary), a new x-ray cell for pressures up to about 700 bar is under development at Griffith University.

The collaborators will synthesise light-element materials and study them with powder diffraction, aiming to elucidate the reaction mechanism and pathway. Materials of initial interest include $\text{Li}^{11}\text{BD}_4$, $\text{Mg}^{(11}\text{BD}_4)_2$ and the suspected intermediate or “sink” compounds of the type $\text{MB}_{12}\text{H}_{12}$.

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Project No.

Title: Effect of severe plastic deformation on hydrogen storage behavior

Project Leader: Jacques HUOT (HRI-UQTR) – Canada

International Collaborations: D. Fruchart (CNRS, France), B.C. Hauback (Physics Department, IET), Norway), Dilson Santos (UFRJ, Brazil)

Level of Effort (Duration): 1 py/y (3 years)

Background

In the previous Task 22 project (*Synthesis of metal hydrides by cold rolling and their characterization*) we mainly studied the effect of cold rolling on magnesium-based materials and BCC alloys. We found that, especially for magnesium-based alloys, cold rolling reduces the activation (first hydrogenation) time and could produce nanocrystalline structures with enhanced hydrogen sorption kinetics.

Project Plan

The objective of this project is to get a better understanding of the impact on hydrogen storage behavior of the various SPD parameters. The main SPD technique investigated will be cold rolling but Equal Channel Angular Pressing (ECAP) and High Pressure Torsion (HPT) will also be considered. In the case of cold rolling, we will study the effect of rolling temperature, rolling speed, % of reduction at each rolling pass, and numbers of rolling. The investigation will be on magnesium and magnesium-based alloys.

Effect of temperature

The amount of recrystallization depends on the temperature. In this part of the study, we will investigate the effect of temperature on the crystal structure, mechanical properties and number of defects on cold rolled Mg and Mg-Pd alloys. Rolling temperature will be 77K, 298K, 373K, 473K, and 573K. Samples will be characterized by X-ray powder diffraction, SEM and TEM, and calorimetry. The activation time and hydrogen sorption kinetics will also be measured. This part of the project will be in close collaboration with Dr. D. Santos.

Effect of rolling speed and reduction %

Rolling speed and reduction % has a large impact on the amount of energy and thus number of defects, given to a sample. Also, for binary compounds these parameters may have a large impact on the effectiveness of interdiffusion of the elements. Rolling speed covering an order of magnitude will be studied. For reduction %, we will study reduction at each rolling pass of 10%, 25%, and 50%.

Effect of numbers of rollings

Especially for magnesium and magnesium-based alloys, as the number of rolling increases the material is getting cold worked and is harder to roll. However, for the purpose of hydrogen storage even if the material is pulverized its hydrogen sorption properties may still be excellent. Therefore, we will modify our rolling apparatus in such a way that rolling could be performed even on powder samples. This way, we could investigate the effect of numerous rolling.

Neutron investigation

Selected systems will be investigated by neutron powder diffraction with collaboration of Dr. B. Hauback and Dr. D. Fruchart.

Milestone

Year 1: Effect of temperature on Mg-Pd alloys completed.

Year 2: Effect of rolling speed and reduction % is completed. Results of years 1 and 2 will be combined in order to set the parameters for studying the effect of numbers of rollings.

Year 3: Optimum conditions (temperature, rolling speed and reduction %, and number of rollings) are established for Mg-Pd alloys. Neutron diffraction on selected alloys.

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Project No.

Title: Synthesis and characterisation of light metal hydrides and nano-porous materials.

Project Leader: Torben R. JENSEN (iNANO, Chemistry Department, Aarhus University) – Denmark.

International Collaborations: **1.** Korea Institute of Science and Technology (KIST), Seoul, Korea (YoungWhan Cho). **2.** Institute for Materials Research, Research Centre Geesthacht GKSS, Germany (Martin Dornheim). **3.** Max-Planck-Institut für Metallforschung (MPI), Stuttgart (Michael Hirscher). **4.** Institute for Energy Technology (IFE) Oslo, Norway (Bjørn C. Hauback). **5.** Metallurgy and Materials, The University of Birmingham, UK (David Book). **6.** Nanoscale Science and Technology Centre, Griffith University, Brisbane, Australia (Evan Gray).

Level of Effort (Duration): 1.0 py/y (3 years)

Background

The world's primary energy needs are expected to grow by 45 % from 2006 to 2030 and may be doubled by year 2050. The present energy supply is based on the limited resource fossil fuels, the use of which is causing increasing CO₂ content in the atmosphere and possibly also increasing global mean temperature. Renewable energy in the form of solar, wind or wave energy is an attractive inexhaustible resource, but its utilisation is hampered by its fluctuation in time and non-uniform geographical distribution and most countries need to integrate several contributions. Hydrogen is a world-wide target as a safe, cheap and efficient energy carrier, which receive considerable political and scientific interest. This is the basis for the 'hydrogen' research within Center for Energy Materials (CEM), Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry at Aarhus University (led by Torben R. Jensen).

Our research program is focused on synthesis of novel materials and characterization of chemical, physical and structural properties. We have long experience with a wide range synthetic methods and techniques for physical characterisation. We have developed and implemented new state-of-the-art equipment for *in-situ* synchrotron radiation powder X-ray diffraction (SR-PXD) at the synchrotron radiation source MAX-lab, Sweden for detailed studies of hydrogen uptake and release at variable temperatures and pressures. Fast reactions can be studied, i.e. pressure change over 5 orders of magnitude within seconds.

Project Plans

New synthesis methods were recently discovered in our laboratory, which has led to a range of novel borohydrides. We intend to study structure and properties and hope to tailor other new materials. In some cases borohydrides form eutectic melting mixtures. This will be further explored in collaboration with KIST in order to reduce the hydrogen release temperature. Borohydrides are generally very reactive, which will be utilised for design of reactive hydride composites in collaboration with GKSS. The aim is to introduce a new dehydrogenated state that facilitate rehydrogenation. The materials are characterised using *in-situ* SR-PXD, thermal analysis, Sieverts measurements and solid state CP/MAS NMR at iNANO. Raman spectroscopy will be performed in collaboration with University of Birmingham. Hydrogen release and uptake reactions will be investigated at high pressures, 200 to 2000 bar in collaboration with Griffith University using both X-ray and neutron diffraction.

New potassium aluminium hydrides are prepared at iNANO and characterised in collaboration with IFE. The detailed structure and mechanism for hydrogen release and uptake remains not fully understood. New nano-porous carbon materials are also prepared at iNANO and metal hydrides are successfully imbedded. Gas release properties will be analysed in detail for these materials in collaboration with MPI.

Furthermore, combined gas and solid state hydrogen storage at elevated pressures will investigated in collaboration with KIST and GKSS.

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Project No.

Title: Integrated computational and experimental methods for thermodynamic prediction and kinetic analysis

Project Leader: Tejs VEGGE (Risø National Laboratory for Sustainable Energy, Technical University of Denmark, DTU) – Denmark

International Collaborations:

1)University of Iceland, Science Institute, Iceland (Hannes Jónsson). 2)Institute for Energy Technology (IFE), Norway (Bjørn Hauback). 3)Tohoku University, Institute for Materials Research (Shin-ichi Orimo)

Level of Effort (Duration): 1.0 py/y (3 years)

Background

The activities in the Energy Storage and Conversion group (led by Tejs Vegge) at the Materials Research Division, Risø National Laboratory for Sustainable Energy (DTU) are focused on developing new hydrogen based materials and catalysts for energy storage and electrochemical conversion.

The activities are based on designing new materials from a detailed understanding of the fundamental materials properties, which is obtained using closely integrated computational methods (density functional theory (DFT) calculations and path techniques), and advanced experimental characterization techniques (quasi-elastic neutron scattering (QENS) and small and wide angle X-ray scattering (SAXS and WAXS)) performed under *in situ* conditions.

We work primarily with (complex) metal hydrides, e.g. metal borohydrides, and metal amines for indirect storage of hydrogen in the form of ammonia in metal salts, where we collaborate extensively with the Department of Physics (DTU).

DFT calculations are used to provide information about equilibrium particle shapes, the catalytic effect of dopants, activation energies and rates. Furthermore, we use DFT to analyze and predict the thermodynamic stability of new materials, e.g. ternary and quaternary metal borohydrides. The calculational results then form the basis for analyzing and interpreting our nano-scale characterization experiments as well as our selection of catalysts and materials for synthesis.

Project Plans

The planned activities will primarily focus on the development of new methods and combinations of methods for prediction of thermodynamic properties and accurate assessment of kinetic properties such as diffusion and desorption rates. We will focus on metal borohydrides, metal amines and magnesium based materials for energy storage and battery applications; primary focus will be on tuning the materials properties by alloying and mixing.

In collaboration with Prof. Hannes Jonssons group at the University of Iceland and the Center for Atomic-scale Materials Design (CAMD), we aim to develop a new method (milestone) for assessing potential errors from anharmonic effects on the accurate determination of e.g. reaction rates; a problem which appears to be particularly pronounced in complex hydrogen storage materials.

In collaboration with Prof. Bjørn Hauback group at IFE, we will apply a combination of quasielastic neutron scattering (QENS) experiments and DFT calculations to determine diffusion mechanisms and rates of hydrogen/hydrogen complexes in metal borohydrides (milestone).

Finally, we will perform large-scale screening studies using DFT calculations and database methods to predict optimal materials combinations, e.g. mixed metal borohydride structures for battery application in collaboration with Prof. Shin-ichi Orimo (Tohoku University).

Lab-scale synthesis, X-ray characterization and testing of the most promising materials combinations will also be performed.

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Project No.

Title: TM and RE intermetallics based metal hydrides, from fundamental to processes and storage units

Project Leader: Daniel FRUCHART (Group IICE, Institut Néel, CNRS Grenoble) – France

International Collaborations:

IPHE countries: (A project ECONET, under frame of French Foreign Office has been made: 31/10/2009, concerning partners in 1 and 3.

1/ Russian Universities of Perm (Pr N. Skryabina), St Peterburg (Pr M. Shelyapina), Novosibirsk (Pr I. Konstanchuck) which the IICE-Grenoble (Institut Néel - CRETA) is linked with under a PICS (CNRS-FRBR) scheme (materials and characterization, methods and metallurgy characteristics, granulometry, H- and solid NMR, electronic structure computing)

2/ Kurdymov Institute, Kyev (Pr A. Rud) (material treatments and nanoprocessing)

3/ Erevan University, Armenia (Pr S. Dolukhanian) (catalysts and new materials)

4/ University of Coimbra, Portugal (Pr J. Gil & B. Costa) (PAC and μSR^+ spectroscopies)

IEA countries

5/ UQTR - IRH at 3-Rivières Canada (Pr Huot) (materials, characterization, SPD processes), linked by French-Canadian actions

6/ UFRJ, Rio de Janeiro, Brazil (Pr D. Dos Santos) (SPD techniques), linked by CAPES-COFECUB actions

7/ USCar, São Carlos, Brazil (Pr W. Botta) (SPD techniques and HREM), linked by FAPESQ actions.

8/ IFE, Oslo, Norway (Pr B. Hauback) (high resolution neutron diffraction, SANS), under EC contract schemes (NessHy-NanoHy...)

9/ NCSR-Demokritos, Greece (Pr T. Stubos) (heat of reaction -code and systems-, compressor and other applications) under EC contract schemes (NessHy-NanoHy..... other projects under examination)

Others opportunities for collaboration are now opened with: 10/ Griffith University, Australia (Pr E Mc Gray) (SANS) and 11/ University of London (Pr M. Koudrachova) (atomist. calculations), 12/ ENEA Roma (A. Moreno), (fuel cell materials, SANS), cooperations namely to organize through **IAEA** partnerships with 1-3-5-8-10-11-12

Level of Effort (Duration): 1.5 py/y (3 years)

Background

Background for the work to be done in this project (including some background about your activity in the field etc.). IPHE-projects relationships are specified here above..

To develop new performing materials with high intrinsic properties (high reversible hydrogen uptake, room temperature active, fast hydrogen diffusion) and to optimize the extrinsic properties in view of applications (high reactivity, robustness, at cycles...). Conventional and sophisticated method of characterization will be used for. Emphasis will be made on the use of mechanical techniques allowing deliver appropriated micro-nano structure, leading to high potential performances for application. Applications will be evaluated by developing demonstrators or (and) prototypes comprising tanks.

These activities will be replaced in the present context of activities with various synthesis methods and specific instrumentations (HEBM, ECAP, Rolling, Forging, HF melting, plasma and laser assisted deposits...), determine the characteristics of kinetics and thermodynamic stability (experimentally : DSC, PCT..., theoretically ; electronic structure analysis and MC...), analyze crystal structure and

microstructure (HREM, XRD, ND, texture, grazing, SANS...) to develop really operating materials (to be tested in systems in view of practical uses),

Project Plans

A description of what you plan to work on in the project. Specification of present and expected collaboration should be given. In addition some milestones about the work can also be included

1/ Synthesis of the materials belonging to the here above mentioned 3 classes of materials absorbing noticeable reversibly amounts of hydrogen, (2009-2010)

2/ Determine the crystal structure of the new materials, compounds and their hydrides by using all possible solid state techniques (XRD and X-spectroscopy's, e.g. EXAFS), neutron scattering techniques (diffraction, SANS, QNS...), electron and other microscopy's and micro probing...(2010-2011).

3/ Establish the kinetics and thermodynamics of the H-reacting systems as well as the overall stability of such systems and the related hydrides by computing the electronic properties (ab-initio, DOS, cluster calculations, H-dynamics...) (2010-2011)

4/ Optimize researches and applications in order to install the best conditions of reactivity, namely by using methods and techniques enabling a/ to deliver appropriated micro to nanostructures (e.g. Severe Plastic Deformation and other thermo-mechanical approaches), b/ addition of so-called "catalysts" (fundamental understanding, optimization of interaction for both solid-gas reactions and hydrolysis), c/ to generate valuable bodies of metal hydrides with high heat conductivities close to the hydrogenation/dehydrogenation reactions (2010-2011)

5/ Study and design and optimize systems for applications (tanks, sensors), to connect and test in hydrogen chains (from production to consumption). (2012)

6/ Investigate and identify safety risks to determine rules. Investigate the field of pertinent economical parameters (materials, processes, systems). Evaluate up-scale steps and procedures (2010-2012)

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Project No.

Title: Composite materials combining metallic compounds and porous materials for the chemical or electrochemical storage of hydrogen.

Project Leader: Michel LATROCHE (CNRS ICMPE UMR7182) – France

International Collaborations:

Level of Effort (Duration): 1 py/y (3 years)

Background

Combination of adsorption and absorption processes using chemical reaction in metallic compounds and physical bonding in porous materials leads to enhance hydrogen storage properties in a wide range of pressure and temperature. Such combination has shown the possibility of cooperative effect, especially near room temperature, leading to the conclusions that the hydrogen uptake is larger than that of the components alone¹. Moreover, recent works have shown that very high electrochemical capacities can be achieved using out of equilibrium materials mainly based on magnesium and transition metals. For example, the Mg-based system shows a capacity four times larger than that of classical metal-hydride systems but research on other transition metals are also in progress.

Project Plans

We propose to develop hybrid solutions taking advantages of the two methods, namely ad- and absorption in order to obtain composite materials with large capacities in a wide range of temperature and pressure. Most of the recent works have been devoted to the incorporation of single metallic elements (such as Pd, Pt, Ni) and we want to develop the preparation of new materials made of intermetallic compounds with enhanced storage properties. Such approach has been recently demonstrated² with the synthesis of PdNi alloy nanoparticles in an ordered mesoporous carbon template. We also plan to develop the electrochemical storage of hydrogen through the preparation of highly capacitive materials mainly based on the Mg system but also using conversion reactions between metallic hydrides and lithium³.

This work will be performed in collaboration with different laboratories in France but we also expect interests from other groups from the IEA-HIA (ORNL, USA, Demokritos, Greece, MPI-MF Stuttgart,) as concerns the hybrid materials and Eindhoven University of Technology, NL for the electrochemical materials.

¹Campesi, R.; Cuevas, F.; Gadiou, R.; Leroy, E.; Hirscher, M.; Vix-Guterl, C.; Latroche, M., Carbon, 2008, 46, 206-214.

²Campesi, R.; Cuevas, F.; Leroy, E.; Hirscher, M.; Gadiou, R.; Vix-Guterl, C.; Latroche, M., Microporous and Mesoporous Materials, 2008, 117, 511-514.

³Y. Oumellal, A. Rougier, G. A. Nazri, J-M. Tarascon AND L. Aymard, Metal hydrides for lithium-ion batteries, *Nature Materials* 7, 2008, 916–921.

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Project No.

Title: Kinetic Optimization of $\text{LiBH}_4/\text{MgH}_2$ and $\text{Ca}(\text{BH}_4)_2/\text{MgH}_2$ Reactive Hydride Composites

Project Leader: Martin DORNHEIM (Department of Nanotechnology, GKSS Research Center Geesthacht) – Germany

International Collaborations:

1. iNANO, Chemistry Department, Aarhus University, Denmark (Torben R. Jensen);
2. Institute for Energy Technology (IFE) Oslo, Norway (Bjorn Hauback);
3. Korea Institute of Science and Technology (KIST), Seoul, Korea (YoungWhan Cho);
4. Metallurgy and Materials, University of Birmingham, UK (David Book)

Level of Effort (Duration): 1.0 py/y (3 years)

Background

The department of Nanotechnology at the GKSS Research Center has more than 17 years experience in the production of nano-materials and more than 12 years experience in the area of hydrogen storage in light weight metal hydrides.

In 2004, KIST, HRL Laboratories as well as the GKSS Research Centre discovered the reversible reaction of MgH_2 – borohydride composites under much more moderate conditions than in case of the pure borohydride systems. GKSS could synthesize $\text{MgH}_2 / \text{LiBH}_4$, $\text{MgH}_2 / \text{NaBH}_4$ and $\text{MgH}_2 / \text{Ca}(\text{BH}_4)_2$ by hydrogenation of the respective $\text{MgB}_2 / \text{LiH}$, $\text{MgB}_2 / \text{NaH}$ and $\text{MgB}_2 / \text{CaH}_2$ composites. These composite systems show very favorable thermodynamic properties and very high gravimetric hydrogen storage capacities at the same time. However, in spite of kinetic improvement of these very promising systems by a factor of 10 due to the usage of suitable additives sluggish reaction kinetics maintain a hurdle for lots of technical applications.

Project Plans

In this project the promising composite systems $\text{LiBH}_4/\text{MgH}_2$ and $\text{Ca}(\text{BH}_4)_2/\text{MgH}_2$ with gravimetric hydrogen storage densities of 11.4 wt.% and 8.3 wt.% will be studied by a large variety of methods: Sieverts measurements, high-pressure DSC measurements, in-situ XRD measurements (in cooperation with iNANO and IFE), in-situ Raman measurements (U. Birmingham), TEM (KIST), SANS, SAXS, ASAXS, EXAFS and XANES.

Different reaction paths can occur in these complex systems. Therefore, one important aim of this project is to understand how different reaction paths can be favored and others be suppressed.

Another important aim is the kinetic optimization of these systems, i.e. the lowering of working temperatures.

For optimization of reaction kinetics different approaches will be taken:

- Altering the synthesis routes,
- knowledge based development of suitable additives as well as
- sample pre-treatments.

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Project No.

Title: Synthesis and characterization of new tetrahydroborate compounds and nanoscale hydrides

Project Leader: Maximilian FICHTNER (Karlsruhe Institute of Technology (KIT), Institute for Nanotechnology) – Germany

International Collaborations:

EMPA, Switzerland (A. Züttel); IFE, Norway (B. Hauback); Univ. Tohoku, Japan (S. Orimo); PNNL (E. Rönnebro); KIST, Korea (Y. Cho)

Level of Effort (Duration): 1 py/y (3 years)

Background

We have developed methods for the synthesis of pure borohydrides compounds and for synthesis of fully and partly isotope labeled hydrides. Furthermore we have infiltrated these compounds into micro- and mesoporous scaffolds based on carbon.

For characterization, we have equipment and know-how for structural analysis by single crystal and powder X ray diffraction and for thermal analysis such as TGA-MS, TGA-DTA, and HP-DSC. Mass spectrometric analysis can be used in order to characterize and quantify gaseous by-products of the decomposition reaction. Kinetic and thermodynamic measurements can be performed in a Sieverts apparatus and with thermal analysis methods. Structural analysis is done mainly in collaboration with partners, by synchrotron and/or neutron diffraction.

Project Plans

The goal of the collaboration will be to synthesize and characterize pure boranate compounds and nanodispersed hydrides on the basis of light metals and transition metals as hydrogen carrier materials. The materials will be synthesized in both the protonated and the deuterated and/or ¹¹B labelled form.

Characterization of the pure compounds includes investigation of the structure and the physical and chemical properties of the compounds, with a focus on the stability and the transformation mechanism. Structural analysis will be performed by synchrotron and neutron diffraction. Several ways will be tested in order to examine the effect of dopants to the transformation mechanism. Furthermore, dopants will be investigated on their effect to the kinetics and the formation of volatile by-products.

The investigation of the nanodispersed systems will focus on the investigation of kinetic and thermodynamic effects which may be due to the nanoscale nature of the hydrides and the fact that they are embedded in a nanoporous matrix.

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Project No.

Title: Hydrogen Physisorption on MOFs

Project Leader: Michael HIRSCHER (Max-Planck-Institut für Metallforschung, Stuttgart) – Germany

International Collaborations: Caltech, USA (C. Ahn), University of Birmingham, UK (D. Book), Università di Roma "La Sapienza", Italy (R. Cantelli), Univ. du Québec à Trois-Rivières, Canada (R. Chahine), iNano, Århus University, Denmark (T. Jensen), CNRS Thiais, France (M. Latroche), University of Salford, UK (K. Ross)

Level of Effort (Duration): 0.5 py/y (3 years)

Background

The hydrogen storage group at the Max-Planck-Institut für Metals Research in Stuttgart, Germany, works on hydrogen storage for 20 years. Therefore we have experience in many different classes of solid state materials as metal hydrides, carbons, carbon nanotubes and for more than 5 years we are focusing on the new class of metal-organic frameworks (MOFs). Over the years we have developed several experimental set-ups to determine the hydrogen storage properties of very small samples with high accuracy and gain information on adsorption sites. At the moment we participate in NESSHY project funded by the EU, the Hy-Co network funded by the German Government and a DFG priority program on MOFs.

Project Plan

The aim of this project is to correlate the hydrogen storage properties to the structure of the MOFs and to understand the microscopic nature of the adsorption process. It is well known that the specific surface area correlates linearly to the maximum hydrogen uptake, but which parameter influences the binding energy for hydrogen in porous materials is still subject to discussion. The pressure and temperature dependence of the hydrogen uptake is determined with a manual and two automated Sievert's type apparatus from 77K to room temperature and up to 200bar. From these measurements the isosteric heat of adsorption can be calculated with very high accuracy over a wide range of surface coverage. The adsorption sites for hydrogen are characterized by thermal desorption spectroscopy (TDS). Three TDS set-ups cover the temperature range from 20K to 1000K and measure the desorption temperature of hydrogen to vacuum. In addition, further characterization of the adsorption sites by neutron diffraction and Raman spectroscopy are planned.

A detailed understanding of the structure-property correlation between hydrogen storage and the chemical and textural microstructure will enable a tailored synthesis of materials with optimized hydrogen storage properties.

Furthermore, these MOFs, possessing an ordered structure with well-defined pores, can be used as scaffold and the influence on thermodynamics and kinetics of hybrids of nanocrystalline metals and porous materials will be investigated in cooperation with iNano.

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Project No.

Title: Synthesis and characterization of metal doped carbons

Project Leaders: Theodore A. STERIoTIS and Athanassios K. STUBOS (NCSR “Demokritos”) – Greece

International Collaborations: South West Research Institute, USA (M. Miller), Joint Research Center, Netherlands (P. Moretto), University of Crete, Greece (G. Froudakis), NREL, USA (A. Dillon), University of Nottingham (G. Walker).

Level of Effort (Duration): 1.0 py/y (3 years)

Background

The Porous Media Group of the National Research Center Demokritos, Greece has developed over the last years significant R&D activities related to hydrogen safety studies and hydrogen storage in solid materials. PMG coordinates the European FP6 Integrated Project on Hydrogen Storage in Solids (NESSHY) as well as the Targeted Research Project HyCones and participates in the HySafe FP6 Network of Excellence and the NANOHY FP7 Collaborative project. PMG holds a long-standing and well-established position in the field of synthesis and characterisation of a wide range of nanostructured materials for environmental and other applications with emphasis on inorganic and hybrid porous media with a center of gravity in novel carbon structures (e.g. activated carbons, templated carbons, fullerenes, CNTs, carbon foams etc.). Moreover, the group has been at the forefront of experimental techniques for materials characterisation mostly based on sorption, diffusion and (X-ray and Neutron) scattering techniques. Strong international collaborations (also through EC funded projects) in the field of materials science and technology have led to the development of leading-edge know-how on novel materials synthesis as well as advanced experimental infrastructure. During the last two years the focus has been on synthesis, structural characterization and evaluation of novel alloy-carbogenic foam composites, which revealed strong potential for hydrogen storage applications, while theoretical approaches has provided evidence on the feasibility of storage in such systems.

Project Plans

The high hydrogen storage capacity of the carbogenic foam is presumably based on the so-called spillover catalytic mechanism. This mechanism has not been yet resolved and in this respect PMG aim is to investigate the phenomenon, both experimentally and theoretically. In particular, starting from the available molecular precursor based carbogenic foam, a number of other support-receptor systems (namely a series of templated carbons) will be synthesized and tested for their hydrogen storage properties. The materials will be doped with Pd or Pd-alloy nanoparticles as the original material. Emphasis will be placed on a) enhancing the specific surface area b) increasing the number of active receptor sites (e.g. by progressive surface oxidation) and c) induce appropriate “bridging” between the metal nanoparticles and the receptors. Additionally, it will be attempted to synthesize and test a number of doped foam/MOF composites (in collaboration with the University of Crete, Greece). Furthermore, the use of different alloys is planned in order to assist the investigation of the catalytic mechanisms, especially when coupled with studies on the hydrogenation of bulk phases. For this approach, the original CF support/receptor will be used, while emphasis will be placed on finding dopants that consist of easily available and reasonably priced materials. In terms of characterization, hydrogenation experiments will be coupled with desorption/MS studies, in situ FTIR and neutron (or X-ray) scattering (Diffraction and Inelastic). Finally, a multiscale (atomistic to macroscopic) modeling approach has been developed and will be the basis for understanding the fundamental mechanisms that underlay the spillover phenomenon.

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Project Plan

Project No.

Title: Fundamental and applied hydrogen storage materials development of composite Mg:C materials: Using thin films and post composite processing of ball milled material

Project Leader: Sveinn ÓLAFSSON (Physics department, Science Institute University of Iceland) – Iceland

International Collaborations: Bjørn Hauback IFE.

Level of Effort (Duration): One PhD student (3 years)

Background

SO has extensive 20 years background in the physics of hydrogen in low dimensional structures such as thin films, multilayers and superlattices. During last 3 years his research group has been studying the growth and behavior of hydrogen in Mg:C composite thin films. The latest findings in that work has been that co-sputtered Mg:C films show nano-scale 20-30 nm grain structure intermixed in carbon like network. Upon hydrogenation of Pd capped 100 nm film of $Mg_{0.88}C_{0.12}$ the plateau pressure of hydride formation increases 120 fold at room temperature due to confinement and clamping effects from substrate and the carbon network. This increase in plateau pressure is 60 times large than similar film grown without carbon. Relatively little is still known about stability and structure of such strongly confined Mg grains. Initially the Mg grains show crystalline structure that disappears during hydrogen loading. Formation of the MgH_2 phase has therefore not even been confirmed.

Project Plans

The project plan includes two tasks: One fundamental research task linked to material characterization and stability studies of hydrogenated Mg:C thin films of varying composition. This will be accomplished within two years. The later task will be to develop instrumentation and processes on small scale to form bulk material of Mg:C composite using ball milled Mg material as a source. Standard composite process methods will be tested with assistance and cooperation from Bjørn Hauback's group at IFE Norway. First year will yield the first bulk material samples while second year will give some performance testing and third year second iteration of instrumentation and characterization of bulk samples.

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Project Plan

Project No.

Title: Hydrogen storage in nanostructured complex hydrides, molecular compounds and metal alloys.

Project Leader: R. CANTELLI (Physics Department, “Sapienza” University of Rome) – Italy

International Collaborations: Pacific Northwest National Laboratory (Dr T. Autrey, Dr E. Ronnebro); University of Nevada, USA (Prof. D. Chandra); University of Geneva, Switzerland (Prof. K. Yvon); Savannah River National Laboratory (Dr. R. Zidan), CNRS (Dr. M. Latroche), University College London (Prof. X. Guo), University of California at Santa Barbara (Dr. J. Eckert), Oak Ridge National Laboratory (Dr. C. Contescu)

Level of Effort (Duration): 1.5 py/y (3 years)

Background

The Rome group has 40 years experience in hydrogen diffusion and precipitation, trapping and quantum tunnelling at low temperature, phase transformations. The current studies are concerned with the characterization of complex metal hydrides, interstitial metal hydrides, and molecular compounds, and with novel synthesis procedures. The experimental techniques used are the anelastic spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), mass spectrometry, neutron scattering, and X-ray and neutron diffraction.

In anelastic spectroscopy studies of the dehydrogenation process of undoped and of Ti catalysed NaAlH_4 conducted in collaboration with Prof. C. Jensen of Hawaii University, it was shown that concomitantly with the chemical reactions of dehydrogenation, a highly mobile species containing hydrogen is formed, possibly constituted by a complex of type AlH_{6-x} ($x > 0$); a model was formulated that attributes to Ti a trapping role on hydrogen which decreases its dissociation energy in the bond and makes the decomposition reaction reversible. Compounds of the Li-N-H system have been studied in collaboration with Prof. D. Chandra of University of Nevada. In particular, anelastic spectroscopy and thermogravimetry measurements have been conducted in order to characterize the phase transformations occurring in Li_3N and the heating-induced decomposition reaction of lithium amide (LiNH_2) into imide (Li_2NH). The modulus variation has been used to monitor the time and temperature progression of the decomposition, and showed that the reaction rates are faster than those usually reported.

Project Plans

The ongoing research on ammonia borane (NH_3BH_3), conducted in collaboration with Dr. Thomas Autrey of PNNL, is focused on the nature of the structural phase transformation at 225 K and on the hydrogen dynamics. The kinetics of the transformation, the associated heat exchange and the measurement of the real hysteresis provided new information on the nature of the tetragonal to orthorhombic transition. The thermally activated relaxation processes observed at low temperature were attributed to the torsional and rotational motions of the NH_3 and BH_3 ends of the complex. The collaboration on NH_3BH_3 will continue and the studies will be extended to the thermally induced decomposition process and the effect of the dispersion of AB in porous silica scaffolds. The studies of the local and long-range dynamics of hydrogen, defects and other mobile species, of the phase transformations, and of the role of catalysts in LiBH_4 and $\text{Ca}(\text{BH}_4)_2$ borohydrides, will be carried out in collaboration with E. Ronnebro and D. Chandra. The investigation on aluminium hydrides will be conducted in conjunction with R. Zidan. The study of Pd-containing activated carbon fibers will be carried out in collaboration with C. Contescu. Part of the above activities will be conducted within the framework of a Project recognized by IPHE (coordinated by R. Cantelli). The studies on M-H and M-H₂ interactions in zeolites and chemical hydrides, and the synthesis of novel metal-organic frameworks based on the self assembling of 1st and 2nd row transition metals with N and P will be conducted by an international collaboration between A. Albinati and J. Eckert.

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Project Plan

Project No.

Title: Atomic scale characterization of hydrogen storage materials (metal hydrides, nanoporous materials, clathrates) by optical spectroscopy and neutron scattering techniques.

Project Leader: Marco ZOPPI (Consiglio Nazionale delle Ricerche – Istituto Sistemi Complessi) – Italy)

International Collaborations: ForschungsZentrum Karlsruhe, D (M. Fichtner), ISIS-STFC, UK (A..J. Ramirez-Cuesta), KIST, Korea (Y.W. Cho), Pacific North West National Laboratory, USA (T. Autrey)

Level of Effort (Duration): 1 py/y (3 years)

Background

New materials for hydrogen storage are needed for an effective transition to a Hydrogen Economy. To this aim, the microscopic information on novel substances, both structural and dynamic, is of fundamental importance to understand the interaction of hydrogen with the host at the atomic/molecular level. This, in turn, can give us hints on how to improve these materials or to devise new ones. In this framework, experimental techniques accessing directly the structure and dynamics of condensed matter, at the microscopic level, are essential tools. The research group at CNR-ISC has the needed expertise in the spectroscopic characterization of bulk hydrogen and hydrogen-based materials using light scattering (Raman), infrared absorption, and neutron scattering techniques.

In recent years, we have used our experience to the experimental investigation of hydrogen-containing materials and/or hydrogen-containing mixtures. In this context we have studied liquid and solid mixtures of molecular hydrogen with other molecular systems (including stoichiometric Van der Waals compounds at high pressures), molecular hydrogen confined in a host solid matrix (carbon nanotubes, zeolites, porous materials in general), atomic hydrogen in simple and complex hydrides. In all the cases light scattering and neutron scattering techniques have been extensively used.

In our own laboratory we can study materials under pressure up to ≈ 3 kbar, using “standard” scattering cells, and up to ≈ 1 Mbar, using diamond anvil cells. Samples can be conditioned in any desired atmosphere (using a glove box) and measured in an extensive range of temperatures between the triple point of hydrogen (13 K) and several hundreds of degrees C. Thanks to these techniques, we have been able to synthesize hydrogen clathrates (at $p \approx 2000$ bar and $T \approx 0^\circ\text{C}$) which, in turn, were characterized in an extensive temperature range (from 0°C to 15 K). Raman spectra of metal hydrides, synthesized by collaborating partners, have been measured, *in-situ*, in an extensive range of temperatures (from 15 K to 300°C) and in a controlled atmosphere environment.

Light scattering experiments have been complemented with neutron diffraction, and inelastic neutron scattering experiments, carried out at the pulsed neutron source ISIS (UK).

The interpretation of the experimental data is greatly facilitated by an extensive use of Computer Simulation techniques both in the classical or the quantum mechanical limit.

Project Plans

We will continue and expand our studies of these compounds, concentrating on materials that are most promising for hydrogen storage. These include metal organic frameworks, nanoporous activated carbons, and hydrogen clathrates, as far as molecular storage is concerned.

As for materials able to store hydrogen in atomic form, we have been working on binary hydrides (mainly neutron scattering) and are presently working on complex ternary hydrides (inelastic neutron scattering and Raman spectroscopy) including alanates and borohydrides.

The expertise of our group will be essential to study different materials that will be synthesized by our collaborators. At the same time, we will proceed on our activity on clathrates that can be produced in-house using different guest molecule beyond hydrogen.

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Project Plan FOR EXTENSION

Project No.

Title: Synthesis and Characterization of novel metal hydrides

Project Leader: E. AKIBA (Energy Technology Research Institute (ETRI), National Institute of Advanced Industrial Science and Technology (AIST)) – Japan

International Collaborations: University of Québec at Trois-Rivières (Canada), Prof. J. Huot; University of Bordeaux (France), Prof. J. L. Bobet; Anhui University of Technology (China), Prof. Q. A. Zhang; Los Alamos National Laboratory (USA), Dr. K. Ott; Institute for Energy Technology (Norway), Dr. B. C. Hauback.

Level of Effort (Duration): 1 py / y (3 years)

Background

Japan has a scenario of market introduction of fuel cell vehicles, which was proposed from industry in 2008. Under this scenario, year of 2015 is the target to start market penetration of fuel cell vehicles and construction of hydrogen refueling station. Hydrogen storage on board is still critical issue to realize commercially available fuel cell vehicles. Our approach is based on fundamental study of metallic hydride in order to provide most advanced information to industry that develops materials for on board hydrogen storage.

Under the previous Task 17 activities and on going Task 22, our group has successfully synthesized novel hydrides containing A-H bonding by hydrogenation of Al alloys and novel Mg based BCC alloys. We have characterized these alloys and hydrides using various techniques (mostly in-situ conditions) including X-ray and neutron diffraction/scattering, TEM, positron annihilation and so on.

Apart from IEA activities, our group has a 35-year history on the research of hydrogen storage materials, especially various hydrogen absorbing alloys. We may input some of the results from off-IEA activities to Task 22 if the time and conditions are appropriate.

We have international collaborators as shown above and some others under discussion.

Project Plans

During the extension period of Task 22 we plan to continue the activities of Task 22 but will study various materials using in-situ apparatus including X-ray, neutron, TEM, positron, NMR, etc.

In a past a few year under the Task 22 we have investigated mainly on Mg based BCC alloys prepared using ball milling technique. Crystal structure and local structure of prepared alloys and their hydrides have been investigated using X-ray and neutron diffraction under collaboration with Los Alamos National Laboratory, USA. We have also measured hydrogen capacity, pc isotherm and SEM/TEM images.

We plan to investigate not only Mg based BCC alloys but also other metallic hydrides such as Ti or V-based BCC alloys, Mg-based Laves phase alloys, super structure alloys and others. Under the Japanese HYDRO-STAR project, in-situ neutron total scattering spectrometer NOVA has been installed at J-PARC neutron facility. Next a few years, we will use NOVA for crystal and local structure analysis of metallic hydrides. We have also developed in-situ techniques including positron annihilation, NMR, TEM and SPM under the HYDRO-STAR project. These will be used for detailed characterization of advanced metallic hydrides.

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Project Plan

Project No.

Title: Basic research of non-metallic hydrogen storage materials

Project Leader: Y. KOJIMA (Hiroshima U.) – Japan

International Collaborations: Professor Bjørn C. Hauback (Physics Department, Institute for Energy Technology) – NORWAY, Dr. Anthony K. Burrell (Los Alamos National Laboratory) – USA

Professor Peter Edward (University of Oxford)–UK

Level of Effort (Duration): 1 py/y (3 years)

Background

Hydrogen storage materials have been studied in Institute for Advanced Materials Research, Hiroshima University for a few decades. Recently, much attention has been given to thermal decomposition of metal hydrides with light elements (binary hydrides and complex hydrides) because of their large gravimetric H₂ densities. However, the high work temperature and the slow reaction rate (high activation energy) limit the practical application of the lightweight metal hydride (chemical hydride) systems. We have focused on nano-composite materials to improve those properties. The nano-composite materials for hydrogen storage encompass a catalyst and composite of chemical hydrides at the nanometer scale. The catalyst increases reaction rate. The thermodynamic stability of the nano-composite materials can be controlled by making the composite of chemical hydrides having protide (hydride) (H^{δ-}) and proton (H^{δ+}). In addition, the hydrogen absorption kinetics is accelerated by the nano-size materials and they may change the thermodynamic stability of the materials. Light weight nano-composite materials such as Mg-based nano-composite materials, metal-carbon-hydrogen (M-C-H) system, metal-nitrogen-hydrogen (M-N-H) system and metal-boron-hydrogen (M-B-H) system have been synthesized. We have also reported a new concept of hydrogen storage such as hydride-ammonia (MH-NH₃) system.

Project Plans

The goal of our project is to establish the principle of the basic technology in order to control the kinetics and thermodynamics of the non-metallic hydrogen storage materials having high H₂ capacity. Nano-composite materials, single crystals and thin films based on light elements will be prepared. Thermal analysis [thermogravimetry - differential thermal analysis - mass spectrometry (TG-DTA-MS), differential scanning calorimetry - mass spectrometry (DSC-MS), gas chromatography, CHN elemental analysis], spectroscopic analysis [magic angle spinning-nuclear magnetic resonance (MAS-NMR), X-ray absorption spectroscopy (XAS), Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction(XRD)], microscopic analysis [scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX), scanning tunneling microscopy (STM), optical microscopy], ion beam analysis and neutron scattering will be used for the clarification of structural characterization and hydrogen storage mechanism in the non-metallic hydrogen storage materials. All the above analyses will be performed without exposing the samples to air. In-situ analyses will be also used to characterize the hydrogen storage mechanism. We will collaborate with the other partner of the IEA HIA Annex 22 with structural characterization

(neutron diffraction and scattering, synchrotron X-ray diffraction, electron spin resonance) and the materials properties.

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Project Plan

Project No.

Title: Metal Hydride Synthesis under High-Pressure Hydrogen Atmosphere

Project Leader: Nobuhiro KURIYAMA (UBIQEN, AIST) – Japan

International Collaborations: Dag Noréus (Stockholm University) – Sweden.

Level of Effort (Duration): 1 py/y (3 years)

Background

AIST has found new family of Mg-TM-based metal hydrides, Mg₇ZrH₁₆ etc., under high hydrogen atmosphere over 1 GPa. Those hydrides absorb and desorb hydrogen rapidly around 573K without decomposition of the hydrides into hydrides of their components. Their hydrogen capacity is expected to be 4~6 mass%.

Stockholm University has synthesized novel complex hydrides of transition metals under hydrogen atmosphere, and clarify their structure by means of their specialized X-ray diffraction technique and neutron diffraction.

Project Plans

The following topics will be studied in the extension period:

- 1) Synthesis of Mg-based, Al-based, other novel hydrides with higher hydrogen capacity and lower dissociation pressure under high hydrogen atmosphere,
- 2) Precise structure analysis by X-ray and neutron and evaluation of thermodynamic properties for the synthesized hydrides. These results will be reflected in the strategy for the above synthesis.

AIST will mainly synthesize hydrides and evaluate thermodynamic properties, and Stockholm University will mainly analyze structure of the hydrides.

Synthesis will be conducted from Dec. 2009 to May. 2012, and structure analysis and thermodynamic evaluation will be from May 2010 to Nov. 2012. Final target of this project is to develop metal hydride which desorbs 6 mass% of hydrogen below 373K.

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Project Plan

Project No.

Title: Development of Light-Weight and Compact Hydrides

Project Leader: S. ORIMO (IMR, Tohoku University) – Japan

International Collaborations: A. Züttel (EMPA) – Switzerland, C.M. Jensen (University of Hawaii) – USA, T. Autrey (PNNL) – USA, B. David (RAL, University of Oxford) – UK, T. Vegge (RISO) - Denmark

Level of Effort (Duration): 1 py/y (3 years)

Background

Main topics of our previous projects (H-14 in Annex 17 (2004-2006); “Development of Nanostructured Li-based Complex Hydrides: H-37 in Task 22 (2008-2009); “Development of Light-Weight and Compact Hydrides”) are as follows:

- Suppressing the gas-phase ammonia from the composites of Mg-amide and Li-hydride
- Providing the new pathways for dehydrating reactions of the composites of complex hydrides
- Substituting the *M* elements considering their electronegativities in *M*-amides and *M*-borohydrides
- Searching the intermediate compounds of *M*-borohydrides
- Synthesizing and characterizing the perovskite hydrides
- Clarifying and modifying the thermodynamical stabilities of Al-hydrides

Parts of the topics have been financially supported by NEDO Fuel Cell and Hydrogen Technologies Development Projects “Development of Technologies for Hydrogen Production, Delivery and Storage Systems (2008-)”.

Project Plans

The following 3 topics will be intensively studied in the extension period of Task 22.

- 1) Searching reversibly-formed intermediate phases in *M*-(*M'*-)borohydrides (single- and/or double-cation systems)
- 2) Synthesizing Al-based new hydrides
- 3) Developing engineering-oriented synthesis processes of the *M*-(*M'*-)borohydrides and the Al-based new hydrides

Milestones

Milestone	Month/Year
Searching the reversibly-formed intermediate phases in <i>M</i> -(<i>M'</i> -)borohydrides (single- and/or double-cation systems)	Dec./09 -
Synthesizing Al-based new hydrides	April/10 -
Developing engineering-oriented synthesis processes of the <i>M</i> -(<i>M'</i> -)borohydrides and the Al-based new hydrides	April/11 -
Final conclusion	Nov./12

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Project Plan

Project No. H-13

Title: Synthesis and characterization of complex alloy hydrides

Project Leader: Young Whan CHO (Korea Institute of Science and Technology) – Republic of Korea

International Collaborations: 1. EMPA (Andreas Züttel), 2. Aarhus University (Torben Jensen), 3. Birmingham University (David Book), 4. FZK (Max Fichtner), 5. GKSS (Martin Dornheim), 6. IFE (Bjørn Hauback).

Level of Effort (Duration): 1.0 py/y (3 years)

Background

We have recently studied dehydrogenation/rehydrogenation properties of a complex metal hydride, $\text{Ca}(\text{BH}_4)_2$, as well as reactive hydride composites such as $\text{Ca}(\text{BH}_4)_2+x\text{MgH}_2$, LiBH_4+xMH ($\text{MH} = \text{CaH}_2$, YH_3 , CeH_2), and $\text{LiBH}_4+x\text{Ca}(\text{BH}_4)_2$ systems. The scope of our work covers mechanochemical synthesis of these composite materials, improvement in kinetics using halides of transition and rare-earth metals to form nano-catalysts in-situ, and in-situ observation of dehydrogenation/rehydrogenation reaction pathway. In addition, theoretical studies based on the first-principles and thermodynamic calculations have also been carried out in parallel with experimental works. The results of our studies indicate that a proper combination of different complex hydrides or a mixture of complex and simple binary metal hydrides with an appropriate catalyst may become a promising material for high capacity reversible hydrogen storage systems.

Project Plans

We will carry out both experimental and theoretical studies on the synthesis, characterization, and sorption properties of $\text{Ca}(\text{BH}_4)_2$, LiBH_4+xMH , $\text{LiBH}_4+x\text{Ca}(\text{BH}_4)_2$, and $\text{Ca}(\text{BH}_4)_2+x\text{MgH}_2$, with or without catalytic additives. A dry mechanochemical reaction route will be adopted for the preparation of composite materials, and both hydrothermal and thermal decomposition routes will be adopted for mesoporous materials.

The proposed work will include;

- 1) Phase transformation and dehydrogenation reaction path of $\text{Ca}(\text{BH}_4)_2$
- 2) Structural analysis of several unknown intermediate phases found during the decomposition of $\text{Ca}(\text{BH}_4)_2$
- 3) Evaluation of reaction enthalpies of single- and multi-step decomposition of $\text{Ca}(\text{BH}_4)_2$ by DSC as well as by first-principles calculations.
- 4) Dehydrogenation and hydrogenation reaction path of $\text{Ca}(\text{BH}_4)_2+x\text{MgH}_2$
- 5) Dehydrogenation and rehydrogenation of $\text{LiBH}_4+x\text{Ca}(\text{BH}_4)_2$ system confined in a chemically inert mesoporous material.

We will use DSC, HP-DSC, TGA/MS, XRD, FT-IR, Raman, combined in-situ SR-XRD/PCI, neutron diffraction techniques to investigate the basic sorption behaviour and crystal structure of these hydride systems. The eventual goal of this project is to find a new complex alloy (composite) hydride that exhibits a reversible hydrogen storage capacity of $> 8 \text{ wt}\%$ and the dehydrogenation temperature of $< 300^\circ\text{C}$.

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Project Plan

Project No.

Title: Development of nanocrystalline metal hydrides using vapour deposition technologies

Project Leader: Darius MILCIUS (Centre for Hydrogen Energy Technologies, Lithuanian Energy Institute)– Lithuania

International Collaborations: Stockholm University, Prof. Dag Noreus; Institute for Energy (JRC), Dr. Constantina Filiou;

Level of Effort (Duration): 1 py/y (3 years)

Background

Systems such as Mg₇TiH~16 and Mg₆VH~14 form crystalline compounds with a rather ordered structure but including some vacancies in the magnesium sites. These hydrides can store about 6 wt% of hydrogen and release it at temperatures about 150 C lower than ordinary magnesium hydride. The problem is that they have to be synthesised at extremely high pressures and when they desorb hydrogen, the metal atom structure collapses and the metals segregate. Mg-TM thin films are more amorphous in character, than the high pressure synthesized hydrides. But still they have a cubic atomic structure related to the substructure found in Mg₇TiH~16 and Mg₆VH~14. On the other hand the films seem not to disintegrate when being discharged.

Lithuanian Energy Institute is active in hydrogen storage related projects since 2000. Our current hydrogen storage activities in FP6:

SSA NENNET - High Quality Research Network on Nanosciences, Material and Energy research in Lithuania.

The European Research Training Network (RTN) “Hydrogen Storage Research Training Network” (HyTRAIN)

SSA HYSIC - Enhancing International Cooperation in running FP6 Hydrogen Solid Storage activities.

LEI scientist also participate in Nordic Energy Research Programme (“New metal hydrides for hydrogen storage” 200-2006) and new project proposal: Nordic Center of Excellence on Hydrogen Storage Materials 2007 – 2010.

Project Plans

To continue on magnetron sputtering technique, which can rapidly grow and control the relevant Mg-TM mixture films to a high accuracy, will be used for thin film synthesis. Hydrogenation of thin films will be realized at high pressure after deposition and during grow using reactive deposition in hydrogen plasma, enabling the injection of hydrogen ions, thus simulating a high pressure and directly form hydride films on different substrates.

Milestones:

1. Mg-TM-hydrides produced by magnetron sputtering techniques and high pressure charging of metal films. This will include samples of up to 200 mm³ of Mg-TM composites hydrided for neutron scattering characterization and for electrochemical characterization.
2. Mg-based composite materials with hydrogen absorption capacity over 4 wt% at room temperature.

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Project Plan

Project No.

Title: Synthesis, structural characterization and stability of complex hydrides

Project Leader: Bjørn C. HAUBACK (Physics Department, Institute for Energy Technology) – Norway

International Collaborations: Griffith Univ, Australia (E. Gray), Curtin Univ., Australia (C. Buckley), HRI-UQTR, Canada (J. Huot), Univ. of Aarhus, Denmark (T. R. Jensen), Risø-DTU, Denmark (T. Vegge), CNRS Grenoble, France (D. Fruchart), KIT, Germany (M. Fichtner), GKSS, Germany (M. Dornheim), ETRI AIST; Japan (E. Akiba), Hiroshima Univ., Japan (Y. Kojima, H. Fujii), KIST, Korea (Y. W. Cho), Stockholm Univ., Sweden (D. Noréus), BNL, USA (J. Graetz), Univ. of Hawaii, USA (C. Jensen) PNNL, USA (E. Rönnebro), SRNL, USA (R. Zidan).

Level of Effort (Duration): 2.0 py/y (3 years)

Background

The Physics Department at Institute for Energy Technology (IFE) has been involved in fundamental studies on hydrogen storage materials for several decades. During the last years the focus has been on synthesis, structural characterization and stability of complex hydrides. Our research has in particular been focused on alanates, amides/imides systems, Mg-based hydrides alane and borohydrides. The Physics Department is responsible for the neutron-based materials research in Norway using the research reactor JEEP II located at IFE. Thus, the combination of broad expertise in neutron scattering and basic knowledge of structure-property relationships in hydrogen storage materials is important for our participation in Task 22. In particular the high-resolution powder neutron diffractometer, PUS, is important for studies of hydrogen storage materials, and during the next year two more powder neutron diffractometers will be in operation at IFE. We also possess a broad expertise in X-ray scattering techniques (including synchrotron radiation) in general, and use both standard and synchrotron X-ray diffraction routinely. Different ball-milling equipment, hydrogenation setup and equipment for thermal analysis (DSC, TPD, PCT) are available in our laboratory. In particular based on our access and competence in diffraction techniques, we are part of many projects involving international collaboration.

Project Plans

The project will address both synthesis and advanced characterization of metal hydrides based on Al, B, N and Mg. Reactive ball-milling (in H₂-atmosphere) and cryomilling in addition to standard room-temperature ball milling will be used both for preparation of new compounds and for introduction of additives. The use of neutron scattering is a very important tool for structural characterization of hydrogen storage materials. The powder diffractometer PUS can be used for experiments at temperatures between 7 and about 1400 K. In addition an *in-situ* cell optimized for hydrogen/deuterium is available for experiments up to 10 bar pressure and 1400 K. We have routinely access to synchrotron X-ray diffraction at ESRF in France, and the combination of neutrons and X-rays is very useful for detailed structural studies. Stability and kinetics will be studied by using accurate Sievert apparatus. Very important we will also contribute to the other partners of the IEA HIA Task 22 with structural characterizations (including neutron high-resolution and *in-situ* experiments and synchrotron X-ray high-resolution and time-resolved *in-situ* studies) of different types of novel metal hydrides.

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Project Plan

Project No.

Title: Stability and Reversibility of Borohydrides for Hydrogen Storage

Project Leader: Andreas ZÜTTEL (Empa Materials Science and Technology, Dübendorf) – Switzerland

International Collaborations: Shin-Ichi Orimo (Tohoku University, Sendai, Japan), Maximilian Fichtner (FZK, Karlsruhe, Germany), Bernard Dam (Vrije Universiteit, Amsterdam, The Netherlands), Martin Dornheim (GKSS, Hamburg, Germany), Dag Noreus (Stockholm University, Sweden).

Level of Effort (Duration): Empa group: 2 py/y; overall: approx 12 py/y (3 years)

Background

This project is part of an international collaboration on Borohydrides as reversible hydrogen storage materials, which involves both IEA- and IPHE-affiliated researchers. The participants are: Shin-Ichi Orimo (Tohoku University, Sendai, Japan), Maximilian Fichtner (FZK, Karlsruhe, Germany), Bernard Dam (Vrije Universiteit, Amsterdam, The Netherlands), Martin Dornheim (GKSS, Hamburg, Germany), Dag Noreus (Stockholm University, Sweden). The participants bring to the project relevant expertise at the highest international level in theory and modelling, materials synthesis, structural studies, characterisation of thermodynamic properties related to hydrogen storage materials and the elucidation of reaction mechanisms in complex hydride systems.

Tremendous progress has been made in the past few years on reversible hydrogen storage in complex hydrides, particularly on the catalysis and reversibility of Na[AlH₄], and the physical properties, e.g. stability of Li[BH₄]. Seminal contributions have been made by members of this collaboration.

The goal of the collaboration will be to explore the liquid borohydrides as hydrogen storage materials using hydrogen/deuterium isotope labelling. Furthermore, to synthesise new compounds from the elements and to investigate the physical properties, especially the stability, and to develop models for the mechanism of the formation, decomposition, and for the stability. The mobility and direct environment of the hydrogen in the lattice as well as the coexisting ions will be investigated in detail and modeled.

Project Plans

The main elements of the collaborative research plan are:

- focus on areas where we have world-class expertise, namely complex hydride structures and properties and the thermodynamics of complex hydride dehydrogenation and hydrogenation reactions;
- thermodynamic parameters for the reversible hydrogen sorption;
- explore the field of light elements for new liquid phases and compounds;
- Study the mobility of the hydrogen and ions in complex hydrides to unravel the formation/decomposition mechanism of the borohydrides.

A survey of the state of knowledge in the field showed that much more work is needed to understand the reaction mechanisms by which the hydrogenation and dehydrogenation of complex hydrides occur. Therefore a significant theoretical and experimental effort will be directed at reaction mechanisms and the stability of the intermediate and final products.

The Empa group will focus on the determination of the synthesis and stability of the (liquid) borohydrides and the mobility of the hydrogen in the complex hydrides.

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Project No.

Title: Hydrogen storage in borohydrides and light-metal hydrides

Project Leader: David BOOK (Metallurgy and Materials, University of Birmingham) – UK

International Collaborations: KIST, Korea (YoungWhan Cho); Aarhus Univ, Denmark (Torben Jensen); EMPA, Switzerland (Andreas Züttel); GKSS (Martin Dornheim); IFE, Norway (Bjorn Hauback); TU Delft, Netherlands (Bernard Dam)

Level of Effort (Duration): 2.0 py/y (3 years)

Background

The Hydrogen Materials Group (www.hydrogen.bham.ac.uk) in the University of Birmingham has over 30 years experience in the investigation into, and the exploitation of, hydrogen–materials interactions. Research areas have included microstructural processing of functional materials using hydrogen, dense-metal membranes for hydrogen separation, and solid-state hydrogen storage. Recent hydrogen storage research topics include: investigation of PGM & LiBH₄-treatment on the H₂ sorption kinetics of milled Mg (FUCHSIA); characterization of porous materials, including zeolites (Bham-Chem), Polymers of Intrinsic Microporosity (Cardiff & Manchester Uni's), and MOFs (NESSHY); the development of a hydrogen powered canal boat (Rex Harris' PROTIUM project, with a metal hydride store from Andreas Züttel); and the synthesis and characterization of metal borohydrides.

Synthesis equipment includes: ball- & cryomills; arc-melter; magnetron sputterer; rapid solidification; high-pressure hydrogenator. While characterization facilities include: 3 Hiden IGAs; 3 Sievert's PCTs (inc. 2 x Hiden HPTs); TGA–Mass Spec; TPD–Mass Spec; 150 bar DSC; in situ Raman spectroscopy and XRD (100 bar cells); and confocal laser microscope (1 bar cell).

Project Plans

Two principal areas will be investigated:

1) ***Synthesis and characterization of Borohydride-based materials***

We will synthesize mixed-metal borohydrides (e.g. Zn- and Mn-based) by ball-milling alkali-metal borohydrides and metal chlorides, and by high-pressure processing of boride/hydride mixtures. The hydrogen storage and microstructural properties of the resulting materials (together with MBH₄/MgH₂ reactive hydride composites from partners) will be characterized.

There will be a particular emphasis on in situ Raman Spectroscopy studies to study the decomposition and recombination behaviour of the borohydride-based materials from Bham and partners. Studies to date on the decomposition of LiBH₄ and LiBH₄/MgH₂ have shown that amorphous decomposition products such as the Li₂B₁₂H₁₂ phase can be detected in situ (at temperature). These studies will complement in situ XRD (Bham) and SR-PXD (Aarhus Univ, IFE) measurements, in helping to identify alternative (reversible) reaction pathways.

2) ***Fabrication and characterization of Mg-based multilayers***

Mg/Ti/Mg multilayers (~1 μm total thickness) have been fabricated by magnetron sputtering onto glass substrates, and it has been demonstrated that Sieverts-PCT and in situ XRD systems can be used for the direct characterization of the hydrogen cycling behaviour. We will use a new configuration of our magnetron sputtering system, to fabricate Mg/TM/Mg (TM = Transition Metal) multilayers with layers <20 nm. We will investigate the effect of interlayer (TM), substrate type, and dimensions of the layers. The effect of using a Pd capping layer on top of the multilayer, will also be assessed.

National collaboration with: Bham-Materials (Paul Anderson), Nottingham-Materials (Gavin Walker), ISIS-RAL (Bill David), and other UK-SHEC partners; Salford (Keith Ross); and Warwick (Mark Smith).

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Project No.

Title: Synthesis, structure, stability and simulation of novel complex hydrides

Project Leader: William I F DAVID (ISIS, STFC) – UK

International Collaborations:

Tom Autrey & Ewa Rönnebro (Pacific Northwest National Laboratory, USA), Shin-ichi Orimo (Tohoku University, Sendai, Japan), Dag Noreus (Stockholm University, Sweden), Torben Jensen (University of Aarhus, Denmark), Andreas Zuttel (EMPA, Switzerland), Evan Gray (Griffith University, Australia)

Level of Effort (Duration): 1 py/y (3 years)

Background

The ISIS Facility at the Rutherford Appleton Laboratory is currently the world's most powerful spallation neutron source. In the field of hydrogen storage, structural characterization plays a key role in the understanding of the mechanisms involved in the reversible hydrogenation and dehydrogenation processes, leading to improvement and potential prediction of material properties. Thanks to the high sensitivity to light elements like hydrogen, neutrons are an ideal probe for a comprehensive characterization of the most promising candidate materials for hydrogen storage, to study both (1) structure and microstructure through combined gravimetric analysis and diffraction, and (2) motion dynamics and energy barriers through inelastic scattering coupled with simulation. Simulation is a central component of our work and is underpinned by Density Functional Theory (DFT) program developers at RAL. High throughput robotic synthesis and characterisation facilities at RAL also enable numerous new materials and catalysts to be screened. The co-location of neutron diffraction (ISIS), X-ray synchrotron diffraction (Diamond), high throughput synthesis and characterisation, and materials modelling (CASTEP development) at the Rutherford Appleton Laboratory enables a comprehensive program in hydrogen storage materials to be undertaken from materials synthesis to full in-situ characterization of and hydrogen absorption and desorption.

Project Plans

Our plans include both hydrogen storage materials discovery and characterisation and methodological advances. In the area of materials discovery, we will work with PNNL in the area of complex molecular hydrides that include derivatives of ammonia borane and also frustrated Lewis acid/base systems. With Aarhus, EMPA and Sendai, we will develop new borohydride systems using the high throughput apparatus at RAL while with Stockholm, we will study fluoride-based MgH_2 derivative systems. In-situ neutron and X-ray diffraction studies will be performed at Diamond and ISIS on key systems - methodological advances in these areas will be undertaken in collaboration with Aarhus and Griffith Universities. Specific milestones include the commissioning of the rapid throughput facility at RAL in the first year and the development of in-situ facilities at Diamond.

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Project Plan

Project No.

Title: Tailoring reaction routes for metal and complex metal hydrides

Project Leader: Prof. Zheng-Xiao GUO (University College London, London) – UK

International Collaborations:

Level of Effort (Duration): 2 py / y (3 years)

Background

For the last several years research on complex hydrides (such as metal nitrides, metal borohydrides, metal amidoboranes etc.) has attracted a significant amount of interest due to their potentially very high hydrogen storage capacity. Typically however these materials suffer from disadvantages that prevent current utilization in technological applications, mainly relating to reusability and the kinetics and thermodynamics of hydrogen release. Independent research from a number of labs has found that some of these properties may be tuned, for example, the heat of formation of metal borohydrides is dependent on the electronegativity of the metal cation, or that the addition of a light metal atom modifies the hydrogen storage properties of ammonia borane (NH_3BH_3). The mechanisms (*e.g.* a determination of the full reaction pathway) behind these improvements have not been fully explicated nor generalized to other systems. As many groups perform research on metal borohydrides and related systems, there are obvious synergies between independent research programmes. Collaborative investigation will aid in understanding the desorption mechanism and the effects of dopants in these systems, with the added value of cross-fertilization of ideas and innovation. We will seek to understand the fundamental mechanisms of hydrogen storage in these systems, and determine the best system for reversible hydrogen storage, which is likely to be a compromise between storage capacity, kinetics, and cost.

Project Plans

The aim of the UCL group is to perform *ab initio* simulations on candidate metal borohydrides (*e.g.* Group I and II borohydrides) and metal-doped amidoboranes (*e.g.* LiNH_2BH_3 , $\text{Ca}(\text{NH}_2\text{BH}_3)_2$) in order to fully understand their hydrogen release properties, and then design specific formulations to speed up practical development. The objectives to achieve the proposed aim are:

1. Model and understand the crystal structure and ground state properties of the borohydride and amidoborane systems
2. Determine full reaction path, including transition states and potential sideproducts, of the dehydrogenation process.
3. Evaluate thermodynamics and kinetics for H_2 desorption
4. Consider effects of cation and/or functional anion dopants on thermodynamics
5. Draw up potential one- and two-parameter descriptor curves relating thermodynamics to electronic structure, in order to provide general predictions for potential new borohydride-related hydrogen storage materials and optimal dopants.

Added benefits will come from sharing information and direct comparison of hydrogen release properties and the effects of interactions with different systems. The Task Workshops will be used a forum for discussing the latest results and coordinating collaborative activities (*e.g.* independent verification of effects of dopants). The list of collaborators below is based on those submitting complex hydride projects to Task 22.

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Project Plan

Project No.

Title: Neutron scattering and ab initio investigations of hydrogen storage materials

Project Leader: Keith ROSS and Ian.MORRISON (Centre for Materials and Physics Research, University of Salford, Manchester M5 4WT) – UK

International Collaborations: University of Stockholm: Prof Dag Noreus; University of Eindhoven: Prof P. Notten; Caltech: Profs Brent Fultz and Channing Ahn; PNNL: Dr Tom Autrey; Prof Shumao Wang: GRINM, Beijing; Prof. Jun Chen:U of Nankai(INEMC); Danesh Chandra: University of Nevada.

Level of Effort (Duration): 3 py/y (3 years)

Background

The work at Salford falls into two topics; the first (Keith Ross, Dan Bull, David Moser, Daniel Roach, Igor Shabalin) involves the use of neutron scattering and direct microbalance measurements to understand the binding of hydrogen in hydrogen/metal and H₂/carbon/Li compounds. Neutron scattering includes in situ diffraction to study the location of hydrogen(deuterium) during hydrogen cycling, Small Angle Neutron Scattering to study the porosity of carbons, incoherent inelastic scattering from hydrogen to study vibrational modes and coherent inelastic scattering from deuterium in complex hydrides to identify modes from their form factors. In the theoretical project (Ian Morrison, Alan Oates, Duncan Riley, Dan Bull and David Moser), ab initio calculations match the experimental measurements in that they predict the hydrogen-metal potential energy surface in a metal and the interaction between molecular hydrogen with carbon and MOFs.

Project Plans

In neutron scattering developments, we will further extend the scope for in situ cycling of samples during ND measurements by developing an internally coated V cylindrical sample. We will investigate the laser ablation of Al internally inside the cylinder. Quasi-elastic neutron scattering will be used to investigate the librational motions of H in imides and amides and possibly long range diffusional motions. Following the success at ISSP (HySIC) in producing Mg₇TiH_x and our recent partially successful preparation in situ on the PEARL neutron diffractometer at ISIS, we will continue our inelastic and quasi-elastic scattering measurements on hydrogen in this system to test the ab initio predictions of multiple site occupation. The INS measurements on presumably atomic H produced by spillover catalysts on carbon foams and IRMOF-8 will be resumed when large enough samples of definite activity become available. Using parallel funding from EPSRC, we will continue to develop the polyCINS technique and will apply it to understanding the D-vibrations in MgD₂ and then the more complex systems such as NH₃BH₃ where the coherent inelastic scattering should considerably extend what can be measured using Raman techniques to identify librational, torsional and vibrational modes. -With respect to the in situ thermodynamic and kinetic measurements, using dry loading, an inert gas glove box and Dynamically Sampling Mass Spectrometry, we will extend earlier measurements on the production of NH₃ in the Li/N/H system.(Nesshy)

In addition to this work, we will continue a current project on the preparation of hybrid carbon frameworks doped with Li₃N. This involves the production of a hyper-cross-linked polymer and pyrolysing it in an air-free pyrolyser under nitrogen. Li is then introduced via an organometallic. We are also using Small Angle Neutron Scattering and contrast matching to study the nature of the porosity in activated carbons. (Joule/NWDA funding)

On the theoretical side, we will continue to use state of the art simulation methodologies for the prediction of the structural and dynamical properties of the complete range of materials being considered within

NESSHY. The investigation of absorption in spillover materials will continue with studies of the changes of release temperature associated with atomic hydrogen absorption as a function of organic linkers in MOFs, these studies will be performed using the DFTB approach benchmarked against the more accurate plane wave pseudopotential approach. Further efforts will be made to understand and model the spillover mechanism (USAL, NCSR-D-Univ. Crete). Related prediction of inelastic neutron scattering spectra will be extended to a larger family of MOFs. The symmetry constrained optimization algorithm will be used to investigate the observed broken symmetries in the Mg-Ti-H system. Rate calculations will be performed to study transport processes in selected complex hydrides. Study of hydrogen storage properties of larger Al clusters (more than 50 Al atoms) will be undertaken to further assess the effect of nanostructure on release temperature. Even larger Al clusters will be studied using the improved H-Al EMT potential. The simulated Al-C nano-textured material, formed by phase separation from a random mixture using DFT calculations, will be used to study the hydrogen uptake and release in confined nano-scale Al clusters. Extended long time scale simulations of hydrogen diffusion in metals at high H-atom concentration will be performed with a view to simulating hydride formation. Application of the combined Ab initio/CALPHAD approach will continue in order to study the phase diagram of the Mg-Ni-Ti system and its hydride and investigate phase stability in the bulk. The CALPHAD approach is also being used for the $\text{Li}_3\text{N}/\text{Li}_2\text{NH}/\text{LiNH}_2/\text{NH}_3$ system and preliminary studies on the effect on the thermodynamics of nanoscale materials will be continued. **(NESSHy funding)**

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Project No.

Title: Porous Materials IEA Collaboration

Project Leader: Gavin S WALKER (School Mechanical, Materials and Manufacturing Engineering, University of Nottingham) – UK

International Collaborations: See below.

Level of Effort (Duration): 0.1 py/y (2 years)

Background

There has been much controversy in some of the claimed hydrogen uptakes for porous materials. The IEA collaboration has been an excellent forum to discuss measurement issues in an attempt to remove some of the ambiguities in measuring and reporting hydrogen capacities. The collaboration also provides independent verification for hydrogen uptake behaviour. A collaborative approach to investigating and understanding the interaction of hydrogen with porous systems will have the added value of cross-fertilisation of ideas and innovation, access to a wider range of characterisation facilities and comparison of hydrogen-metal-carbon interactions for different systems. Through the collaboration, the partners would seek to identify the best porous materials for use in hydrogen stores.

Project Plans

The aim is to investigate metal-carbon porous hydrogen storage systems and to probe the interaction of hydrogen with these materials to fully understand and explore the potential of porous materials for hydrogen storage applications. The objectives to achieve the proposed aim are:

1. Prepare a range of novel porous samples.
2. Independent verification of hydrogen uptake properties
3. Measure hydrogen interactions for the different systems
4. Theoretical modelling of hydrogen interactions with porous materials.
5. Determine the potential for porous materials as viable hydrogen storage media.

Added benefit will come from sharing samples and direct comparison of hydrogen uptakes and interactions with the different systems. The Task Workshops will be used a forum for discussing the latest results and coordinating collaborative activities (e.g. independent verification of uptakes, comparison of hydrogen interactions with different materials). The list of collaborators below is based on the carbon projects being submitted for Task 22. Project leaders of any additional porous material projects accepted for Task 22 will be invited to join the collaboration.

Collaborators and Potential Contributions

Chahine (Canada)	Nanopore C prep and charac.	Ross (UK)	Inelastic neutron scattering
Cantelli (Italy)	Anelastic energy loss spec	Walker (UK)	Porous carbons
Zoppi (Italy)	Raman and ND	Ahn (US)	Characterisation
Guo (UK)	M-graphene modeling	Gallego (US)	M-ACF prep and charac.
Morrison (UK)	Ab initio modeling	Zidan (US)	M-fullerene prep, char, modeling
Hirscher (G)	Characterisation	Book (UK)	Characterisation
Latroche (France)	MOFs	Kim (Korea)	Nanotubes

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Project No.

Title: Multicomponent hydride systems

Project Leader: Gavin S WALKER and David M GRANT (School Mechanical, Materials and Manufacturing Engineering, University of Nottingham) – UK

International Collaborations: Torben Jensen, David Book, Daniele Colognesi.

Level of Effort (Duration): 2.0 py/y (2 years)

Background

The challenge for solid state hydrogen storage materials is designing a system with a high gravimetric capacity, favorable thermodynamics and fast enough kinetics so that the material can operate at temperatures between 80 and 120°C, delivering 1 bar of hydrogen. Multicomponent systems have the promise of modifying the thermodynamics and kinetics of a high capacity phase through the incorporation of a second phase which can help to destabilize or catalyze the hydrogenation/dehydrogenation of the first phase. Our work on lithium borohydride has elucidated the dehydrogenation mechanism of LiBH₄-MgH₂ systems and we have proved that the reaction products formed follows the same generic reaction, although the precise reaction path appears to change with stoichiometry with an intermediate borohydride species appearing to form for the 2:1 mixture [1]. Stoichiometry was also found to affect the hydrogenation kinetics, with magnesium rich mixtures having faster cycling kinetics. The formation of borohydride intermediates is the subject of current investigations along with investigating new destabilized multicomponent hydride systems.

Project Plans

The challenge is to probe and understand the reaction path during the decomposition and formation of the LiBH₄ phase in order to better understand the rate limiting factors for cycling the LiBH₄-MgH₂ systems. In addition to this new destabilization reactions are being investigated with low dehydrogenation temperatures. This work will utilize thermogravimetric and volumetric and mass spectrometric techniques to monitor the dehydrogenation and hydrogenation reactions (under both isothermal and isobaric conditions). *In situ* diffraction techniques will be used to follow structural changes during reactions to identify the reaction mechanism. Collaborators include Jensen (Aarhus) for *in situ* XPD, Book (Birmingham) with *in situ* Raman and Colognesi (CNR) with neutron spectroscopy.

Milestones	Month
Determined intermediates of LiBH ₄ -MgH ₂ hydrogenation	12
Investigated novel destabilization agents for LiBH ₄	18
Investigated non-LiBH ₄ multicomponent systems	21
Determined the reaction pathway for selected novel multicomponent systems	24

Reference

1. G S Walker, D M Grant, T C Price, X Yu and V Legrand, *J. Power Sources*, **194**, 1128-1134 (2009).

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Project No.

Title: High pressure ambient temperature hydrogen storage adsorption

Project Leader: Joseph REITER and Channing AHN (Jet Propulsion Laboratory and California Institute of Technology) – USA

International Collaborations: University of Quebec, Trois Rivieres, Richard Chahine.

Level of Effort (Duration): 0.25 py/y (3 years)

Background

While low temperature physisorption at 77K is deployable for engineering systems at present, alternatives that may obviate the need for such low temperatures would still be of compelling interest for stationary and mobile applications. Data has emerged recently that suggests that zeolite-templated carbons (ZTC's) may offer some advantage over normal super-activated carbons* for ambient temperature applications at the 35 bar pressure that is presently used in test and lease fuel cell vehicles.

We have reproduced the gravimetric and volumetric data from that manuscript below. *Hiroto Nishihara, et al "High-Pressure Hydrogen Storage in Zeolite-Templated Carbon," *J. Phys. Chem. C* 2009, 113, 3189–3196.

While this represents an area of interest in its own right, and while we are presently optimizing our own ZTC's for work in this area, we have plans to further develop materials based on ZTC's in order to improve the isosteric heat from similarly structured materials.

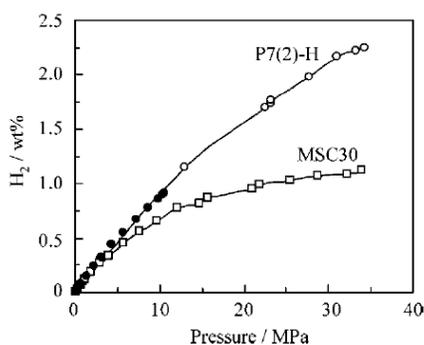


Figure 8. Hydrogen adsorption isotherms of (○) P7(2)-H and (□) MSC30 up to 34 MPa, measured at 30 °C by using an adsorption apparatus constructed for use under above 10 MPa. (●) Isotherm data of P7(2)-H shown in Figure 4a.

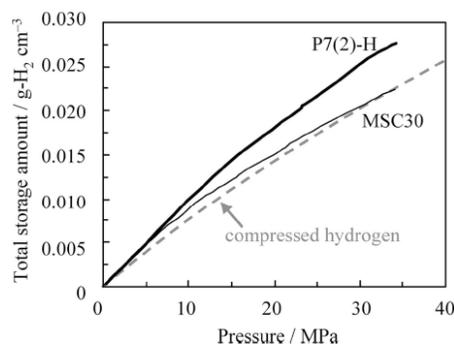


Figure 9. Plot of total volumetric storage amount of P7(2)-H and MSC30 against hydrogen pressure at 30 °C. (---) Amount for compressed hydrogen.

Project Plans

Substitutional doping of carbon with beryllium, boron, and other light elements by solid-state diffusion is recognized as a promising route toward increasing hydrogen binding energy. In particular, computational analysis shows that the strongly localized empty p_z orbital at a Be or B site substituted within a graphite-like surface interacts with the occupied orbital of H_2 , leading to a partial charge transfer from H_2 to the surface. Significantly higher hydrogen binding energy (~ 11 kJ/mol) has been reported experimentally for boron-doped carbon (BC_x) materials, though surface areas in these systems are currently limited to <1000 m^2/g as discussed previously. In addition, on the basis of work at PSU and NREL, hydrogen uptake is found to be $\sim 50\%$ greater in microporous BC_x materials than in carbonaceous materials of similar surface area. Compounds of beryllium-doped carbon are expected to have even higher hydrogen binding energy, but are unknown experimentally.

In practice it has been difficult to obtain boron substitutional levels in carbon greater than ~ 10 wt% by standard synthesis techniques. Graphite-like BC_3 , however, has been known since the late 1980's, when it was first synthesized by John Kouvetakis et al. at Lawrence Berkeley labs. This material has the highest B/C ratio of any such compound, but has only been synthesized as thin sheets on the walls of a tube furnace. This sheet morphology had been viewed by us as a deficiency, resulting in low surface area materials of limited practical use. However, now given our present ability to produce ZTCs, and given the possibility of forming large micropore volume in ZTCs relative to activated carbon, we feel that the use of the templating approach in the synthesis of BC_3 still offers the possibility of an exciting class of microporous sorbents with high B/C ratios can be prepared and investigated as hydrogen storage materials. As part of our effort for Task 22, we plan to:

- 1) Fabricate BC_3 -like microporous material by performing the same reaction as prescribed by Kouvetakis et al., except inside the channels of a typical large pore zeolite as in ZTC. A large variety of such materials could be made by changing the synthesis temperature (to tune the B/C ratio) and the zeolite template (to obtain different porous structure). The reactants, boron trichloride and benzene, are both readily adsorbed by zeolites used in similar ZTC syntheses. Based on the characteristics of ZTC analog materials, this approach should yield amorphous BC_x ($x \sim 3$) materials with ultra high surface area, large microporous volume, and extraordinary hydrogen binding energy.
- 2) We will evaluate gravimetric hydrogen capacities and hydrogen adsorption enthalpies for these BC_x materials, by measuring hydrogen adsorption isotherms at various temperatures. The information gained from these experiments would then be used to refine the synthetic approach with the goal of optimizing the performance of these materials.
- 3) Before the end of this project, we hope to assemble a "bare-bones" Sieverts systems that will be capable of handling 350 bar pressures so that we can verify the literature results. As of now, no lab in the US is capable of doing volumetric measurements at this high a pressure.

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Project No.

Title: Controlled synthesis of metal hydride nanoclusters

Project Leader: Mark D. ALLENDORF (Sandia National Laboratories) – USA

International Collaborations: Name of institutions, name of groups.

Level of Effort (Duration): 4.25 person years, 3 years

Background

The overall objective of this project is to achieve tunable thermodynamics for high-gravimetric-capacity hydrogen storage materials by creating and stabilizing nanoparticles with controlled size, composition, and properties. Some of the most attractive storage materials, such as MgH_2 , AlH_3 , and LiBH_4 , have unfavorable H_2 desorption thermodynamics and are either too stable (e.g. MgH_2) or too unstable (e.g. AlH_3) in bulk form to be practical, particularly for vehicular transport applications with on-board refueling. However, recent theoretical and experimental results indicate that decreasing particle size can substantially reduce the stability of metal hydrides, leading to lower desorption temperatures. This task addresses the three key challenges: 1) the need for synthetic routes that provide controlled nanoparticle size and composition; 2) the need to stabilize nanoparticles against agglomeration and irreversible reaction; and 3) inaccuracies in computational tools used to guide synthesis that can accurately address particle sizes spanning the micro-to-meso length scales. Our project team includes investigators at University of Missouri, St. Louis (Prof. Eric Majzoub) and MIT (Prof. Jeffrey Grossman). During the past year we synthesized several nanotemplates based on metal-organic frameworks (MOFs) and block copolymers (BCP) and successfully infiltrated them with metal hydrides. Kinetics experiments demonstrated destabilizing of NaAlH_4 supported on a MOF and suggest that both size and chemical environment are important factors to be considered when designing templates for this purpose. Computational investigations at MIT also demonstrated that significant, non-systematic, errors are present in the results of density functional theory calculations, and that these errors scale with cluster size.

Project Plans

The technical goals of this project are: 1) to synthesize nanoscale particles of hydrogen storage materials, controlling both size and composition, to yield narrow distributions in the size range for which deviations from bulk thermodynamic properties are either predicted by theory or suggested by experiments; and 2) systematically probe the effects of size and composition to determine the onset and extent of nanoscale effects on the thermodynamics and kinetics of hydrogen sorption.

During the life of this project we plan to do the following:

- Create nanoparticles of hydrogen storage materials with controlled size and composition using BCP, MOFs, and related templates. This will enable pore sizes in the $\sim 1 - 20$ nm range to be accessed, allowing us to identify the transition from bulk to non-bulk properties through desorption experiments. Efforts will focus on materials with the highest potential storage capacities, namely LiH , MgH_2 , LiBH_4 , LiAlH_4 , and $\text{Ca}(\text{BH}_4)_2$.
- Evaluate both gas-phase and liquid-phase infiltration methods.
- Develop methods for compositional tuning, i.e., creating mixed-metal hydride clusters
- Determine the hydrogen desorption kinetics of infiltrated templates, using Simultaneous Thermogravimetric Modulated-Beam Mass Spectrometry (STMBMS), a unique Sandia tool designed to probe thermal decomposition of solids
- Predict nanoparticle composition and thermodynamics as a function of size to guide synthetic efforts, using a suite of computational methods benchmarked against highly accurate Quantum Monte Carlo calculations.

During the course of this work we plan to collaborate with Prof. William David (Oxford University) to probe the interactions between hydride nanoclusters and the template using unique neutron spectroscopy tools available in his laboratories. Finally, we initiated discussions with Prof. Richard Chahine (Institut de recherche sur l'hydrogène, Université du Québec Trois-Rivières, Canada) concerning structural aspects of MOF templates at the Paris Oct. 2009 meeting and will identify complimentary aspects of our research that can result in mutually beneficial collaborations.

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Project No.

Title: Chemical Hydrogen Storage

Project Leader: Tom AUTREY (Fundamental Science, PNNL) – USA

International Collaborations: Italy, Cantelli (University Rome), Zoppi (CNR); UK, David (RAL), Japan, Orimo (Tohoku University); USA, Jensen (University Hawaii), Graetz (BNL), Dedrick (SNL).

Level of Effort (Duration): 2 py/y (3 years)

Background

PNNL is pursuing fundamental and mechanistic studies on hydrogen rich compounds using experimental spectroscopy and computational molecular dynamics approaches. Chemical compounds of interest are composed of light elements and activate hydrogen heterolytically through di-hydrogen bonding interactions.

Our principal interest is in the chemical and physical properties of chemically bonded hydrogen in materials containing both hydridic (H-) and protic (H+) hydrogen. It is our contention that materials composed of Lewis acid-base pairs activate hydrogen heterolytically. Our research group has focused on how the interactions between protonic and hydridic hydrogen in condensed phase affect the structure and dynamics of materials. Understanding the chemical and physical properties of these chemical complexes has important implications to hydrogen activation and hydrogen storage. We use a variety of spectroscopic approaches to understand the fundamental properties of dihydrogen bonding interactions. We use in-situ multinuclear NMR and Raman spectroscopic methods to study mechanisms and the kinetics of hydrogen release in parallel with calorimetry methods to determine thermodynamic properties of hydrogen storage materials.

Project Plans

- Collaborative efforts with Rosario Cantelli, University Rome and with Bill David, Rutherford Appleton Laboratory will be carried out to study the properties of ammonium borohydride. The compound, $[\text{NH}_4][\text{BH}_4]$, a proto typical Lewis acid/base pair is unstable at room temperature.
- Collaborative efforts with Shin-ichi Orimo, Tohoku University and Craig Jensen, University of Hawaii will be carried out to study the mechanism of borohydride decomposition and identify key species important to reversible hydrogen storage.
- Collaborative efforts with Jason Graetz, BNL, will be carried out to study the properties of coupled endothermic and exothermic hydrogen storage materials for hydrogen release and regeneration. We will investigate kinetics and thermodynamics of alane/ ammonia borane composites.
- Collaborative efforts with Marco Zoppi, CNR, and Rosario Cantelli will be carried out to study the properties of ammonia borane at metal oxide interfaces using vibrational and anelastic spectroscopy.
- Collaborative efforts with Dan Dedrick, SNL, will be carried out to study the reactivity of ammonia borane with a goal to understand the mechanisms of gas impurity formation using TG/MS approaches.

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Project No.

Title: Effect of Gaseous Impurities on Long-Term Thermal Cycling/ Aging and Fundamental Studies of Complex Hydrides for Hydrogen Storage

Project Leader: Dhanesh CHANDRA (University of Nevada, Reno (UNR)) – USA

International Collaborations:

IEA/IPHE collaboration with Prof. Rosario Cantelli University of Rome: Anelastic spectroscopy of Amides/imides, $Li_{3-x}NH_x$, with University of Rome (Prof. Rosario Cantelli) was are in progress which were started a few years ago. This research will be also devoted to the possible quantum tunnelling of H in Li_2NH and to the study of Li ion vacancy diffusion in Li_3N . Finally, the mechanisms of the hydrogenation/dehydrogenation reactions will be investigated.

IEA Collaboration Prof. Klaus Yvon, University of Geneva: We are actively working on amide systems. A new solid solution region with intermediate compound have been discovered and characterized by x-ray diffraction. In addition, we are providing insights into the crystal structure (UoG) and thermodynamics (UNR), in particular making ternary phase diagrams and heat capacity (UNR).

IEA Collaboration Dr. Michel Latroche, CNRS, Paris: We are studying destabilization of amide –imide system by using transition metals. We have developed a method to introduce transition metals in the Li_3N that allow creating defects in the structure due to difference in ionic charge. We also have joint work with University of Geneva-UNR-CNRS on this subject. In first week of Dec. 2009 we have beam time at ESRF France synchrotron facility to high resolution work on the samples already prepared at CNRS, Paris. We will examine these samples at Uni. of Rome, and JPL/Cal Tech - NMR studies.

Level of Effort (Duration): xx py/y (3 years)

Background

We propose continuation of the IEA project that we started on imide-amide and other systems to evaluate effects of long-term cycling/aging with impurity gases, under MHCoe project. We also performed fundamental studies on evaluating thermodynamic properties such as phase Equilibria, developing ternary phase diagram of Li-N-H system, predominance diagrams (PN2 vs. PH2), measuring vaporization thermodynamic using torsion effusion measurements, and heat capacity measurements. Pressure cycling apparatuses were constructed at UNR for hydrogen loading and unloading. The overall approach to performing cycling on currently reversible complex hydrides such as imide/amide systems (using Li_3N as precursor), including Li amide-alanate, which has a theoretical hydrogen capacity ranging from 7 to ~10.5 wt% H. The specific tasks were to determine the changes in the pressure-composition isotherm (PCI) after cycling with impure hydrogen. A reference temperature of 255°C and a hydrogen pressure range from vacuum to 2 bar was chosen based on the pioneering research of Prof. Ping Chen's *Nature* paper.

The hydrogen release proceeds by the reactions $Li_3N + 2H_2 \leftrightarrow Li_4NH \rightarrow Li_2NH \rightarrow Li_3N_2H_3 \rightarrow LiNH_2$. Note the well known formation of LiH phase with pure H_2 , that can be prevented with nitrogen compensation; N_2 - H_2 mixtures (new results from IEA studies). We have shown that LiH phase can be prevented and ~ 10 wt% of hydrogen is absorbed; in effect increased the capacity from 6.5 to ~10 wt.%H. These reactions are realistically reversible ~200 °C. The partial substitution of Li lowers the desorption temperature. Moreover, great attention is devoted to mixed systems made of amides and magnesium hydride, which show promising thermodynamic and kinetic properties. The species driving the hydrogenation/dehydrogenation reactions are not quite known, and phase transitions of the starting materials or their interaction with impurity gases need more work; in particular effect nitrogen gas mixed with hydrogen.

Advancements- UNR Project:

1. An important cycling advancement on cycling was use of nitrogen-hydrogen which showed significant improvement in the cycling ability, improving the hydrogen loading to ~10 wt.%H in amide-imide system. These have implication for other system that have amide component.
2. Found new intermediate cubic phase $\text{Li}_3\text{N}_2\text{H}_3$ has NH/NH₂ coordinations between Li_2NH - LiNH_2 ; modeling of new phases with CNRS Li_4NH and $\text{Li}_3\text{N}_2\text{H}_3$
3. Determined the effects of impurity gases that has undesirable effect in varying degrees; using industrial grade hydrogen by subjecting these materials to 1,100 cycles at 255°C with gaseous impurities (O₂, CO, H₂O, and others). Kinetic analyses were also performed on the cycled samples. The rate constant $k(\text{s}^{-1})$ varied by an order of magnitude as the sample was cycled from 1 to 1,100 cycles. We determined rate of degradation was a little lower with alanate-amide samples with impurity gas.
4. Ternary phase diagrams of Li-N-H system, predominance diagrams developed. Measuring heat capacity of the amide-imide materials.
5. Measured vaporization of impurity gases that are evolved during desorption by torsion effusion method, Li_3N , $\text{Mg}(\text{BH}_4)_2$
6. Anelastic properties of imide-amide system
7. Measured Phase transitions in $\text{Ca}(\text{BH}_4)_2$, $\text{Li}_3\text{N}-\text{H}_2$ – in-situ synchrotron x-ray diffraction studies.

Project Plans:

Our plans are to continue the work that we have been doing over the last few years. We are focused on the imide-amide research. But recently many studies are in progress where the amide is mixed with alanate and other compounds. The studies related to imide-amide system have implications in studies of other system. Here is brief summary of the proposed work for the IEA.

1. To evaluate details of N₂-H₂ systems on amide-imide system; effect of Li and N deficiency in the structure as a function of hydrogen loading.
2. Continue ternary diagram (experimental and CALPHAD modelling) studies. We need to measure heat capacities of three of the compounds
3. To measure vapour pressure of LiNH_2 and other compounds by torsion effusion method.
4. Effect of pressure on kinetics of imide-amide system (relates to other compounds that are being currently studied by other groups).
5. Cycling results under hydrogen pressure.
6. Anelastic studies on new compounds (Li-N-H system)
7. Defect structure studies; includes development of synthesis methods to introduce defects in the structure of materials, x-ray diffraction characterization, NMR etc. (JPL-CalTech)

Potential New Collaborations: Dr. Bjorn Hauback (Norway); to work on the imide-amide systems with catalysts.

Dr. Ian Morrison (UK): Yet to be decided

Dr. A. Zuttel's (group) EMPA- Switzerland: Measurement of Heat capacity measurement (UNR) and possible inelastic scattering (EMPA).

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Project Plan

Project No.

Title: Metal-assisted hydrogen uptake on nanoporous carbon materials

Project Leader: Nidia GALLEGO (Oak Ridge National Laboratory) – USA

International Collaborations: M. Latroche - CNRS (France); R. Cantelli - Univ. Rome (Italy); D. Colognesi – CNR (Italy)

Level of Effort (Duration): 0.5 py/y (3 years)

Background

During 2006-2009, Project N-22 of Task 21 was focused on understanding atomistic mechanisms that promote enhanced hydrogen uptake by Pd-modified activated carbon fibers. The project consists of three research aims: theoretical modeling, materials synthesis, and complex characterization using advanced techniques. The modeling effort identified the effect of interlayer spacing between graphite sheets on the hydrogen uptake and the role of stacking sequence on the binding energy of physisorbed hydrogen.¹ Material synthesis has been directed at obtained Pd-modified activated carbon fibers (Pd-ACF) with Pd nanoparticles embedded in a carbon matrix with a large volume of nanopores with optimum width (0.6-0.8 nm) for maximum physisorption interaction.² It was determined that H₂ uptake at room temperatures on Pd-ACF is enhanced compared with Pd-free ACF. The enhancement was attributed to hydrogen spillover from Pd hydride destabilized by contacts with the nanoporous carbon support,³ followed either by chemisorption of H atoms to surface carbon atoms⁴ or recombination to form physisorbed hydrogen.

Project Plans

The project will continue with an effort to develop atomistic models that realistically describe isotropic nanoporous carbons at the atomic and molecular level, and to understand the effect of synergistic interaction between metals and nanoporous carbon on the hydrogen storage capacity. The project will be focused on three different aims: (1) Modeling and characterization of medium-range order in partially amorphous – partially graphitic structures of nanoporous carbons; (2) understanding the mechanisms of molecular activation of hydrogen by metal particles; (3) elucidation of the energetics and dynamics of hydrogen species confined in the molecular space of pure- and metal-doped nanoporous carbons.

The scope of the research project will be enlarged and will comprise nanoporous carbon modified with metals known for catalytic activity in hydrogen reactions, formation of hydrides, or strong polarization effects.

Collaborators

T. Egami (U. Tennessee – USA) – quantitative structure characterization of nanoporous carbons

K. van Benthem (U.C. Davis – USA) – high resolution electron microscopy

M. Latroche (CNRS – France) – synthesis and adsorption properties of metal-doped nanoporous carbons

R. Cantelli (U. “Sapienza” Rome, Italy) – characterization of self-diffusion properties of H atoms

D. Colognesi (Istituto dei Sistemi Complessi Firenze, CNR – Italy) – quasielastic neutron scattering

¹ Aga RS, Fu CL, Krcmar M, Morris JR. The effect of graphite interlayer spacing on hydrogen absorption. *Phys Rev B* **76** (2007) 165404

² Wu X, Gallego NC, Contescu CI, Tekinalp H, Bhat VV, Baker FS, Thies MC., Edie DD: The effect of processing conditions on microstructure of Pd-containing activated carbon fibers, *Carbon* **45** (2008) 54-61

³ Bhat VV Contescu CI, Gallego NC: The role of destabilization of palladium hydride on the hydrogen uptake of Pd-containing activated carbon, *Nanotechnology*, **20** (2009) 204011

⁴ Contescu CI, Brown CM, Liu Y, Bhat VV, Gallego NC: Detection of hydrogen spillover in palladium-modified activated carbon fibers during hydrogen adsorption, *J. Phys. Chem. C* **113** (2009) 5886-5890

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Project Plan

Project No.

Title: Regeneration of Kinetically Stabilized Hydrides

Project Leader: Jason GRAETZ (Energy Sciences and Technology Department, Brookhaven National Laboratory) – USA

International Collaborations: Institute for Energy Technology (Norway), B. Hauback and V. Yartys; Université de Genève, K Yvon.

Level of Effort (Duration): 3 man-months/year (3 years)

Background

The kinetically stabilized metal hydrides offer a new approach to automotive hydrogen storage. The low heat of reaction and rapid hydrogen evolution rates at low temperatures are ideal for mobile PEM fuel cell applications. However, a critical challenge exists to regenerate or recycle these hydrides from the spent fuel and H₂ gas in a low cost and low energy process. Extremely high pressures are required to reform these hydrides by direct hydrogenation and therefore, costly organometallic processes are typically used to prepare these materials. Alternative, low energy regeneration pathways are currently being developed that use complexing agents (e.g. amines) to stabilize the hydride at low pressure. In a subsequent step the stabilized adduct is separated at low temperature to recover the metastable hydride.

Recently we have demonstrated a low energy route to regenerate the kinetically stabilized hydrides LiAlH₄ at low pressure without the need for mechanical milling (J. Graetz, *et. al*, *JACS*, **130** 17790 (2008)). In this process the hydride is stabilized as a THF adduct (LiAlH₄·4THF) followed by a low temperature desolvation step to recover crystalline LiAlH₄.

Project Plans

In this project we will use a similar two-step regeneration process to regenerate aluminum hydride and other kinetically stabilized hydrides. The regeneration process will involve initially forming the hydride as a stabilized intermediate followed by adduct separation and hydride recovery. For AlH₃, this procedure involves the direct formation of an alane amine (AlH₃-NR₃), where alane is stabilized by a nitrogen bond, followed by decomposition and AlH₃ recovery. One task under this effort will be to examine many different amines to determine which ligands are most amenable to forming the alane adduct by direct hydrogenation. A second task will be to explore the separation of various alane adducts to determine which complexes can be separated without loss of hydrogen. This second task will likely involve a transamination step that will be used to exchange one amine for another that forms a less stable adduct. This two step regeneration procedure may be broadly applicable to other metastable hydrides (e.g. Mg(AlH₄)₂) and the third task will be to explore regeneration of other aluminum based hydrides.

Previous efforts have involved collaborations with Bjorn Hauback and group members (Institute for Energy Technology (Norway)) to determine the crystal structures of the beta and gamma phase of aluminum hydride (H.W. Brinks, *et al.*, *J. Alloys Compd.*, **441** 364 (2007) and H.W. Brinks, *et. al*, *J. Alloys Compd.*, **433** 180 (2007)). Further collaboration with this group is expected as we synthesize alane and alanate adducts and undergo an effort to determine the crystal structures of these new materials. Previous efforts have also involved collaborations with Klaus Yvan and group members (Université de Genève) to investigate oxidation and hydrolysis reactions of alane when exposed to air studied by in situ synchrotron radiation.

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Project Plan

Project No.

Title: International Standardized Practices and Materials Development for Hydrogen Storage

Project Leader: Dr. Karl J. GROSS, H2 Technology Consulting LLC – U.S.A.

International Collaborations: multiple Task 22 experts as reviewers.

Level of Effort (Duration): 1 py/y (3 years)

Background

An important goal of Annex 22 and the international hydrogen energy community in general is the development of hydrogen storage materials that meet or exceed the requirements for practical hydrogen storage including stationary applications. There is a strong need to have common metrics and best practices for measuring the practical hydrogen storage properties of new materials that are being developed around the world. This is particularly true at this stage with respect to properties that will impact the engineering design of complete storage/energy generation systems. New categories of materials (ionic liquids, endo/exothermic composites, slurries...) and new expertise are now addressing the challenge of hydrogen storage. This project is creating a reference resource to the hydrogen storage materials development community to aid in clearly communicating the relevant performance properties of new materials as they are discovered and tested. Among other things, this reference details the common pitfalls and many caveats in making materials performance measurements. This project will also include the development of more efficient and accurate analytical methods to speed up the process of materials development and characterization. In addition, novel concepts for hydrogen storage will be explored.

Dr. Karl Gross is very experienced in the development of new hydrogen storage materials, fundamental and applied measurements of the hydrogen storage properties of materials, and the development of complete applied hydrogen storage systems.

Since the beginning of task 22, this project has been very successful in the creation and distribution of a “Best Practices” document. This is a living document which continues to be updated with additional chapters and information relevant to the most current research developments. An important goal of this project is to stimulate international collaboration in the development and review of this reference document.

Project Plans

This project is focused on creating a reference guide of common methodologies, protocols and improvements for measuring critical performance properties of advanced hydrogen storage materials. The work is being accomplished through a combined approach of documenting the experience the project participants have with these measurement, reviewing and incorporating examples from the literature, when necessary, performing experimental measurements to demonstrate important issues, and finally, condensing key information into a concise reference guide. There has been participation from other experts in the field for input, relevant examples, and critical review. Current collaborations with more than 18 experts in the field including 6 IEA Task 22 experts have already been established and will continue within the framework of this project. The project is organized according to the following series of tasks:

- Thermodynamic Stability (2010)
- Cycle-life Properties (2010)
- Materials Heat Transfer Properties (2011)
- Scale-up Materials Performance Properties (2011)
- Total System Engineering Performance Properties (2012)

IEA Hydrogen Implementing Agreement
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Project Plan

Project No.

Title: Novel borohydrides for hydrogen storage

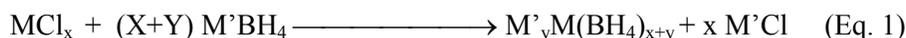
Project Leader: Craig M. JENSEN (University of Hawaii) – USA

International Collaborations: Prof. Bjorn Hauback, Institute for Energy Technology, Norway; Prof. Evan Gray, Griffith University, Australia; Prof. Shin-ichi Orimo, Tohoku University, Japan; and Prof. Torben Jensen, Aarhus University, Denmark.

Level of Effort (Duration): 1.5 py/y (3 years)

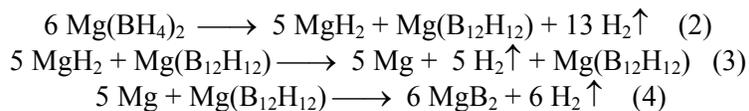
Background

As part of our IEA Task 22 activity, we have synthesized a variety of Group I salts of anionic transition metal borohydride complexes such as: $MM'(BH_4)_x$ ($M = Li, Na, \text{ and } K; M' = Sc, Ti, V, Cr, Fe, Mn, Co, Ni, Cu, Zn, \text{ and } Zr$) through ball milling mixtures of transition metal chlorides and Group I borohydrides as seen in equation 1.



We have characterized the novel complexes by solid-state MAS ^{11}B NMR and examined their hydrogen release and possible reversible uptake by thermal programmed desorption studies. We have found that some of the borohydride complexes such as $Na_2Mn(BH_4)_4$ undergo rapid dehydrogenation at moderate (<130 °C) temperatures while evolving high (>3 wt%) of hydrogen and only very minor the amounts of the undesirable, diborane side product. In an IEA collaboration with researchers at the University of Geneva (Switzerland), the complexes: $MSc(BH_4)_4$ ($M=Li, Na, \text{ and } K$) have also been characterized through infrared and Raman spectroscopy. In a further expanded IEA collaboration with researchers at the University of Geneva, the Institute for Energy Research (Norway), and Aarhus University (Denmark), the molecular structure of the scandium complexes have been determined through synchrotron power X-ray diffraction studies. The lithium salt was the first of this class of compounds to have its structure definitely determined. The diffraction studies confirmed the asymmetric η^3 -coordination of the BH_4 ligands that was predicted by the spectroscopic studies.

A second portion of our IEA research project that was carried out in a IEA collaboration with E. Rönnebro (presently at Pacific Northwest National Laboratory), led to the finding of conditions whereby it is possible to accomplish the reversible hydrogenation of MgB_2 to $Mg(BH_4)_2$. We have cycled ~ 12 of the theoretical 14.8 wt % hydrogen that is available through the dehydrogenation pathway seen and equations 2-4 and its micro-reverse.



Project plans

1) In collaboration with the Institute for Energy Research (Norway), and Aarhus University (Denmark), we plan to continue to determine the molecular structures of anionic borohydride complexes such $Na_2Mn(BH_4)_4$ and $Li_2Zr(BH_4)_6$ which have demonstrated promising dehydrogenation behavior.

2) In collaboration with IEA participants: Tohoku University (Japan); Griffith University (Australia); and Pacific Northwest National Laboratory (USA) we plan to continue our studies of the reversible dehydrogenation of $Mg(BH_4)_2$ utilizing MAS ^{11}B NMR. We also plan to characterize and quantify the intermediate boranes that are present following the partial dehydrogenation of $Mg(BH_4)_2$ at ~ 250 °C as well as those present after subsequent re-hydrogenation. These studies will entail the aqueous exaction of the boranes and their identification through high-resolution solution ^{11}B NMR spectroscopy. Finally, we plan to continue the study the direct hydrogenation MgB_2 to $Mg(BH_4)_2$ through high pressure in situ X-ray and neutron diffraction studies. These studies will allow the elucidation of the mechanism(s) of the solid state dehydrogenation and re-hydrogenation of $Mg(BH_4)_2$ and reveal if it can be reversibly dehydrogenated to borane species under practically viable conditions.

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Project Plan

Project No.

Title: Discovery and development of borohydride related materials

Project Leader: Ewa RÖNNEBRO (Pacific Northwest National Laboratory) – USA

International Collaborations: R. Cantelli, University of Roma, Italy, W. David and M. Jones, STFC/Oxford, UK, M. Fichtner, Forschungszentrum Karlsruhe, Institut für Nanotechnologie, Germany, E. Gray, Griffith University, Australia, B. Hauback, IFE, Norway, D. Noréus, Stockholm University, Sweden, A. Züttel, EMPA, Switzerland.

Level of Effort (Duration): 1 py/y (3 years)

Background

Dr. Ewa Rönnebro has for more than 15 years been focusing on hydrogen storage materials discovery, synthesis, development and characterization by using X-ray, neutron, TGA/DSC, MS, and Sievert's apparatus. Materials investigated included complex metal hydrides, alloy-type hydrides, Mg-based materials, alanates, amides, and more recently borohydrides and amidoboranes. By taking the approach of hydrogenating known, or presumed, decomposition products of hydride materials, promising candidates can be identified for reversible reactions. The need for light-weight, high-capacity materials has shifted our focus from metal hydrides to metal borohydrides (i.e. Li, Ca, Mg). Although these materials can store ca 11-19 wt% hydrogen, the operation temperatures are high for automotive applications and re-hydrogenation kinetics is slow. Teaming with Prof. Eric Majzoub of University of Missouri, St. Louis, who developed the PEGS-method for theoretical identifications of solid-state crystal structures, we have found promising candidates and reaction pathways. We have identified pathways for direct hydrogenation of calcium and magnesium borohydrides from their end-decomposition products at 700-900 bar H₂-pressures and 300-400°C according to: $2\text{CaH}_2 + \text{CaB}_6 + 10\text{H}_2 = 3\text{Ca}(\text{BH}_4)_2$ and $\text{MgB}_2 + 4\text{H}_2 = \text{Mg}(\text{BH}_4)_2$, opening the door to potential high-capacity hydrogen storage applications. Under certain conditions intermediate species are formed, which may limit reversibility. Spectroscopy; NMR, Raman, FTIR, has become an important tool to identify these species and PNNL has a variety of high-quality instruments for ex situ and in situ analysis. PNNL labs have equipment for solid state and solvent based synthesis, including a high-pressure station <1000bar and <450°C. Our partner's expertise on different characterization methods will complement PNNL's work.

Project Plan

We propose to undertake a study of hydride materials that have potential to meet the US DOE performance targets by teaming with domestic and international partners. Although promising reversibility was observed for Mg and Ca borohydrides, the reaction mechanisms are still not fully known and we are hoping to reveal the best path to full reversibility with reasonable kinetics within the first year, not excluding other complex hydride materials. For ex situ studies and crystal structure determination from neutron data, we will team with the groups of Noréus and Hauback. Anelastic spectroscopy is underway by Cantelli's group to study phase transitions in situ. To reveal the reaction mechanism during hydrogenation of MgB₂ at high-pressures, in situ studies will be performed with Gray's and Jensen's (U. Hawaii) groups. For studying new composite materials and improvement of performance and impurity levels, Züttel's group has provided borohydride materials. Moving on, we are planning to study new metal-nitrogen-boron-hydrogen compounds teaming with David&Jones and others to complement our XRD and spectroscopy data with high-quality synchrotron and neutron diffraction data. Teaming with Majzoub, computational modeling of solid state phases using a combination of database searching and novel Monte Carlo methods will be used to guide experimental work. Newly developed techniques will be applied to B-N-H containing materials. To enhance performance our materials will be nanoengineered to shape nanostructures of hydride materials and catalysts. Teaming with Fichtner, we will explore nanoscale materials and their new features and also inclusion in different nanoframeworks. The insight into reaction mechanism and study of catalysts impact combined with nanoengineering will get us closer to meet the requirements for applications.

IEA Hydrogen Implementing Agreement
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Project Plan

Project No.

Title: Exploration of lightweight borohydrides for hydrogen storage

Project Leader: J.-C. ZHAO (Dept. of Materials Sci. & Eng., The Ohio State University) – USA

International Collaborations: Forschungszentrum Karlsruhe, Institut für Nanotechnologie (Max Fichtner)

Level of Effort (Duration): 2 py/y (3 years)

Background

The hydrogen storage team at The Ohio State University (OSU) has been exploring metal hydrides as a hydrogen storage material with the aim of finding a high-capacity metal hydride to meet the DOE FreedomCAR system targets. We have participated in IEA Task 17 with a project entitled “Lightweight intermetallics for hydrogen storage” (when the project leader was at GE). This project was also part of the DOE Metal Hydride Center of Excellence. After moving to OSU, the project leader together with Professor Sheldon Shore has established a new hydrogen storage research team. By taking advantage of the synthesis capability and boron chemistry expertise of Prof. Shore’s lab and hydride and characterization capabilities of Prof. Zhao’s lab, the OSU hydrogen storage team has already synthesized several new compounds and have performed characterization of their desorption properties.

Project Plans

Mg(BH₄)₂ is very promising for high-capacity on-board hydrogen storage. It has a very high capacity (14.8 wt.% theoretical and 13.2 wt.% observed so far) and very favorable thermodynamic stability ($\Delta H = 53$ kJ/mole of H₂). Our work and Prof. Orimo’s work have shown that an intermediate MgB₁₂H₁₂ phase appears during the decomposition of Mg(BH₄)₂. This intermediate phase is generally regarded as detrimental to the reversibility of Mg(BH₄)₂. We tried to synthesize single phase, anhydrous MgB₁₂H₁₂, but found that the literature reported process didn’t result in the anhydrous phase. A study was subsequently performed using TGA, IR and NMR to monitor the loss of H₂O and H₂ from Mg(H₂O)₆B₁₂H₁₂·6H₂O to Mg(H₂O)₆B₁₂H₁₂ to Mg(H₂O)₃B₁₂H₁₂ to Mg(μ -OH)₃B₁₂H_x. A manuscript is submitted for publication to report the results in detail.

The OSU hydrogen storage materials research team has synthesized and tested several new compounds for hydrogen storage. This was made possible by the availability of four vacuum wet-chemistry synthesis lines in Prof. Sheldon Shore’s laboratory, a group of dedicated researchers, the unique boron chemistry expertise in the group, and a dedicated hydride testing facility established in Dr. J.-C. Zhao’s laboratory. Close collaboration with ORNL, JPL, Caltech, and NIST made possible effective synthesis and characterization of these compounds.

The materials we are synthesizing and studying including Mg(BH₄)₂, Mg(BH₄)₂(NH₃)₂, Mg(AlH₄)(BH₄), Mg(NH₃)₆B₁₂H₁₂, (NH₄)₂B₁₂H₁₂, Mg(CH₃OH)₆B₁₂H₁₂, Mg(H₂O)₃(CH₃OH)₃B₁₂H₁₂, Li₂B₁₂H₁₂(NH₃)₇, (NH₄)₂B₁₀H₁₀, Na(NH₃)_xB₁₂H₁₂, Mg(H₂O)₆B₁₀H₁₀, Mg(NH₃)_xB₁₀H₁₀, AlB₄H₁₁, Mg(B₃H₈)₂. Several of them are new compounds that were not reported before. A few of these compounds showed endothermic desorption at low temperatures, thus they are good candidates for further study as potential hydrogen storage materials. The following compounds are very worthy of further studies: Mg(BH₄)₂, Mg(AlH₄)(BH₄), Mg(NH₃)₆B₁₂H₁₂, (NH₄)₂B₁₂H₁₂, (NH₄)₂B₁₀H₁₀, Mg(NH₃)_xB₁₀H₁₀, AlB₄H₁₁, and Mg(B₃H₈)₂.

We will perform more detailed study of these compounds for hydrogen storage in collaboration with ORNL, JPL/Caltech, Sandia, NIST and other international partners. We will focus on more promising candidates as the properties of these compounds are tested.

IEA-HIA Task 22
Proposed Applied Sciences Projects
November 2, 2009

E. Gray, Australia	Off-Grid and Remote-Area Electricity Supply With Integrated Hydrogen Storage
D. Anton, USA	Chemical & Thermal Modeling in Hydrogen Storage Systems
D. Mosher, USA	System Engineering for Materials Based Hydrogen Storage
R. Chahine, Canada	Sorption Systems and Materials for On-Board Hydrogen Storage
M. Fichtner, Germany	Hydrogen Storage Systems Based On Complex Hydrides
J. von Colbe, Germany	Hydrogen Storage Tank Development and System Integration Based on High Capacity Solid State Storage Material
N. Kuriyama, Japan	Research, Development and Safety Assessment on Metal Hydride Tanks
D. Grant, UK	Atomization Synthesis of Metal Hydrides in Kilogram Quantities
C. Jensen, USA	Design and Testing of High Capacity Alane and Chemical Hydride Based Hydrogen Storage Systems
Y-W Cho; Korea	Development of Combined Heat and Hydrogen Storage Systems Based on Low-Cost Metal Hydrides
E. Ronnebro, USA	Materials Properties and System Modeling of Hydrogen Storage Candidates for Applications
P. De Rango, France	Large scale MgH ₂ Tanks for Stationary Applications
V. Yartys; Norway	Hydrogen Storage Solutions for Stationary and Mobile Applications: From Materials to Systems
J. Reiter, USA	Undefined
T. Jensen, Denmark	Undefined
Japan	Undefined